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(2) The formation of urea when urethane (or ethyl carbonate) is heated in solution with ammonia is solely dependent on the dissociation of urethane, and is no more than a repetition of Wöhler's synthesis in a modified form.

(3) A comparison of the reaction with the formation of urethane from urea and alcohol supplies evidence which is opposed to the carbamide' formula.

(4) Attention is directed to a rational inference from the facts, namely, that the system $\text{C}(\text{NH}_2)_2$ cannot form part of a stable molecule.

The author desires to express his thanks to Miss M. Coade, B.Sc., for her assistance in conducting part of the experimental work.

UNIVERSITY CHEMICAL LABORATORY,
TRINITY COLLEGE, DUBLIN.

[Received, June 18th, 1918.]

LIII.—*The Abnormality of Strong Electrolytes. Part II. The Electrical Conductivity of Non-aqueous Solutions.*

By JNANENDRA CHANDRA GHOSH.

In a previous paper it has been shown that in aqueous solutions of strong electrolytes, the increase in molecular conductivity with dilution can be accounted for quantitatively on the basis of the following simple assumptions:

(a) Only ions exist in solution, the force of attraction between oppositely charged ions being governed by the law of inverse squares.

(b) In solutions of binary electrolytes, the arrangement of ions is analogous to the marshalling of atoms in a simple cubic crystal, whilst that of the ions in solutions of ternary electrolytes corresponds with the fluor spar lattice.

(c) The oppositely charged ions of a molecule form electrically saturated neutral doublets.

(d) It has been shown that, on the above hypothesis, the work necessary to separate the constituent ions of a gram-molecule of nivalent binary electrolytes to an infinite distance,

$$A = \frac{NE^2 \sqrt[3]{2}N}{D^2\sqrt{V}},$$

where N is Avogadro's number, E the charge on an ion, D the dielectric constant of the solvent, and V the molecular dilution. For a ternary electrolyte like barium chloride,

$$A = \frac{3NE^2 \cdot 2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{3} \cdot \sqrt[3]{V}}$$

(e) From Maxwell's equation of the distribution of velocities, it can be easily proved that the number of free ions in a solution containing a gram-molecule

$$= nN \cdot e^{-\frac{A}{n \cdot E^2}}$$

where n is the number of ions into which a molecule dissociates.

(f) Since molecular conductivity is proportional to the number of free ions, and since $A=0$ at infinite dilution,

$$\frac{\mu_v}{\mu_\infty} = \frac{n \cdot N \cdot e^{-\frac{A}{n \cdot E^2}}}{nN} = e^{-\frac{A}{n \cdot E^2}}$$

In this paper it will be shown that the above equation, which gives very good results in the case of aqueous solutions, can be applied with equal success to non-aqueous solutions of strong electrolytes.

The organic ionising solvents have been arranged by Walden in the following order: (1) alcohols, (2) aldehydes, (3) acids, (4) acid anhydrides, (5) acid chlorides, (6) esters, (7) acid amides and amines, (8) nitriles, (9) thiocyanates, (10) thiocarbimides, (11) nitro-compounds, (12) dimethylnitrosoamine, (13) ketones, (14) *epichlorohydrin* (*Zeitsch. physikal. Chem.*, 1906, **54**, 130). This system of classification will be adhered to in the following pages.

1. Alcohols.

(a) *Methyl Alcohol*.—One of the most trustworthy investigations on the conductivity of electrolytes in methyl-alcoholic solutions is that of Carrara (*Gazzetta*, 1896, **26**, i, 119). The observed values of μ_v in tables I and II are taken from his work. The dielectric constant of methyl alcohol at 20° is 32.5. At 25° it is somewhat less; in the calculations, D has been taken as equal to 31. The solutes in tables I and II are all binary electrolytes, and μ_∞ is obtained from any particular value of μ_v by applying the equation

$$\frac{N \cdot E^2 \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad (1)$$

This particular value of μ_∞ is afterwards utilised to calculate the molecular conductivity at other dilutions. It will be seen

from tables I and II that the agreement between the calculated and observed values of μ_v is very good, both in the case of the binary salts and the acids.

Carrara (*loc. cit.*) has also determined the molecular conductivities of strontium iodide in methyl alcohol at various dilutions. Here we expect the equation for ternary electrolytes:

$$\frac{3N.E^2.2.\sqrt[3]{2N}}{D.\sqrt[3]{3}.\sqrt[3]{V}} = 3RT \log_{\mu_r} \frac{\mu_x}{\mu_r} \quad \dots (2)$$

to hold good. Table III shows how well the calculated values agree with those observed.

TABLE I.

Solvent: Methyl alcohol. T = 25°.

Solute.	μ_{∞} calc. from μ_{128}	$v =$	32.	64.	128.	256.	512.
1. NaI.....	94.0	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 68.9 \\ 68.8 \end{array} \right.$	$\left\{ \begin{array}{l} 73.5 \\ 73.1 \end{array} \right.$	$\left\{ \begin{array}{l} 77.3 \\ 77.3 \end{array} \right.$	$\left\{ \begin{array}{l} 80.5 \\ 79.9 \end{array} \right.$	$\left\{ \begin{array}{l} 83.0 \\ 82.2 \end{array} \right.$
2. NaBr....	91.8	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 67.3 \\ 65.8 \end{array} \right.$	$\left\{ \begin{array}{l} 71.8 \\ 71.0 \end{array} \right.$	$\left\{ \begin{array}{l} 75.5 \\ 75.5 \end{array} \right.$	$\left\{ \begin{array}{l} 78.6 \\ 79.9 \end{array} \right.$	$\left\{ \begin{array}{l} 81.1 \\ 82.8 \end{array} \right.$
3. NaCl ...	90.4	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} --- \\ --- \end{array} \right.$	$\left\{ \begin{array}{l} 70.6 \\ 69.6 \end{array} \right.$	$\left\{ \begin{array}{l} 74.3 \\ 74.3 \end{array} \right.$	$\left\{ \begin{array}{l} 77.4 \\ 78.1 \end{array} \right.$	$\left\{ \begin{array}{l} 79.8 \\ 81.8 \end{array} \right.$
4. KI	102.8	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 75.3 \\ 73.8 \end{array} \right.$	$\left\{ \begin{array}{l} 80.3 \\ 79.5 \end{array} \right.$	$\left\{ \begin{array}{l} 84.5 \\ 84.5 \end{array} \right.$	$\left\{ \begin{array}{l} 88.0 \\ 88.5 \end{array} \right.$	$\left\{ \begin{array}{l} 90.8 \\ 91.0 \end{array} \right.$

TABLE II.

Solvent: Methyl alcohol. T = 25°

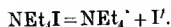
Solute.	μ_{∞} calc. from	$v =$	18.9	37.7.	150.9.
HCl...	$\mu_{27.7} = 157.0$	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 108.4 \\ 106.4 \end{array} \right.$	$\left\{ \begin{array}{l} 117.0 \\ 117.0 \end{array} \right.$	$\left\{ \begin{array}{l} 130.4 \\ 128.0 \end{array} \right.$
HBr...	μ_{∞} calc. from $\mu_{128} = 142.0$	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 6.7. \\ 84.0 \end{array} \right.$	$\left\{ \begin{array}{l} 26.8. \\ 101.9 \end{array} \right.$	$\left\{ \begin{array}{l} 107.4. \\ 113.1 \end{array} \right.$
HI ...	μ_{∞} calc. from $\mu_{11.4} = 152.2$	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 17.9. \\ 104.6 \end{array} \right.$	$\left\{ \begin{array}{l} 71.4. \\ 120.0 \end{array} \right.$	$\left\{ \begin{array}{l} 245.7. \\ 130.5 \end{array} \right.$

TABLE III.

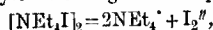
Solvent: Methyl alcohol. T = 25°

Solute.	μ_{∞} calc. from	$v =$	64.	128.	256.	512.
SrI...	$\mu_{128} = 200.4$	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 114.6 \\ 115.3 \end{array} \right.$	$\left\{ \begin{array}{l} 128.6 \\ 128.6 \end{array} \right.$	$\left\{ \begin{array}{l} 141.0 \\ 141.4 \end{array} \right.$	$\left\{ \begin{array}{l} 151.2 \\ 153.5 \end{array} \right.$

The most complete investigation in the field of non-aqueous solutions is that of Walden on solutions of tetraethylammonium iodide in various solvents. It is natural to expect that tetraethylammonium iodide would dissociate according to the following equation:



Except in the case of aldehydes, the variation of equivalent conductivity with dilution calculated from the equation for binary electrolytes (1) does not agree with the observed values. If, however, we assume that tetraethylammonium iodide at first undergoes polymerisation and then the double molecule $[\text{NEt}_4\text{I}]_2$ dissociates as a ternary electrolyte according to the equation:



the calculated values of equivalent conductivities agree extremely well with the observed ones. Indeed, a cursory examination of the data on the variation of equivalent conductivity with dilution will at once lead to the conviction that the electrolytic dissociation of potassium iodide and tetraethylammonium iodide is not of the same type. If it were so, the variation of λ_v (equivalent conductivity) with dilution would have been of the same order. As a matter of fact, whilst λ_v for potassium iodide varies from 80.3 to 84.5 as the dilution increases from 64 to 128, the value for tetraethylammonium iodide increases by 8 units from 83.1 to 91.1 for the same change in dilution. Iodine has a great tendency to form complex ions. We are already acquainted with I_3^- , $\text{I}_3'^-$ ions, etc. It is therefore not at all unreasonable to assume that in tetraethylammonium iodide solutions there exists a complex iodine ion of the type I_2^{--} . Again, the consensus of opinion among electrochemists is generally in favour of complex molecules in non-aqueous solutions. The exact coincidence between the observed and calculated values of equivalent conductivity for tetraethylammonium iodide solutions, as shown in table IV, leaves no room for doubt as to the mode of dissociation of this salt in methyl-alcoholic solution. Of course, the above equation is equally applicable if the salt dissociates, thus:

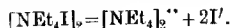


TABLE IV.

Solvent: Methyl alcohol. T = 25°.

Solute.	λ_x calc. from	$V' =$	64.	127.	256.	512.	1024.
NEt ₄ I...	$\lambda_{128} = 130$	λ_v calc.	83.1	91.1	97.7	104.0	108.9
		λ_v obs.	82.1	91.1	98.0	103.6	108.6

In the above table V' is the equivalent dilution.

(b) *Ethyl Alcohol and Propyl Alcohol*.—The dielectric constant of ethyl alcohol at 20° is 21.7 (Walden, *loc. cit.*). In table V the observed values of molecular conductivity are taken from the work of Jones and Lindsay (*Amer. Chem. J.*, 1902, **28**, 341) (*loc. cit.*).

The conductivity of sodium iodide in propyl alcohol has been determined by Schlamp (*Zeitsch. physikal. Chem.*, 1894, **14**, 280). The dielectric constant of propyl alcohol, according to Rudolph, is 13.8.

TABLE V.

Solvent: Ethyl alcohol. $T = 25^\circ$.

Solute.	μ_∞ calc. (equation 1)					
	from	$v =$	64.	128.	256.	512.
KI.	$\mu_{256} = 44.9$	μ_∞ calc.	31.6	33.9	36.0	38.5
		μ_∞ obs.	29.6	33.0	36.0	38.5

TABLE VI.

Solvent: Propyl alcohol. $T = 25^\circ$.

Solute.	μ_∞ calc. (equation 1) from	$v =$	19.8.	55.4.	166.3.	500.
NaI.	$\mu_{166.3} = 176.0$	μ_∞ calc.	79.0	99.5	118.7	135.0
		μ_∞ obs.	77.0	97.1	118.7	138.0

2. Aldehydes.

Acetaldehyde, Propaldehyde, and Furfuraldehyde.—The dielectric constant of acetaldehyde is 21.2, according to Walden, and 18.6 according to Thwing. It is quite probable that the great reactivity of the solvent and its tendency towards polymerisation will completely prevent the formation of complexes in the solute. It is therefore to be expected that here at least tetraethylammonium iodide will dissociate normally as a binary electrolyte. The dielectric constant of propaldehyde is 14, whilst that of furfuraldehyde is 39.4.

TABLE VII.

Solvent: Acetaldehyde. $T = 0^\circ$.

Solute.	μ_∞ calc. (equation 1)	$v =$	100.	1000.	4000.
	from				
NEt ₄ I.	$\mu_{1000} = 178$	μ_∞ calc.	124.0	151.0	160.0
		μ_∞ obs.	122.0	151.0	158.0

TABLE VIII.

Solvent: Propaldehyde. T=25°.

Solute.	μ_{∞} calc. (equation 1) from	$v =$	100.	200.	400.	700.
NEt ₄ I.	$\mu_{200} = 127.6$	$\left\{ \begin{array}{l} \mu_{\infty} \text{ calc.} \\ \mu_{\infty} \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 81.0 \\ 79.8 \end{array} \right.$	$\left\{ \begin{array}{l} 89.0 \\ 89.0 \end{array} \right.$	$\left\{ \begin{array}{l} 95.8 \\ 94.5 \end{array} \right.$	$\left\{ \begin{array}{l} 101.8 \\ 103.9 \end{array} \right.$

TABLE IX.

Solvent: Furfuraldehyde. T=25°.

Solute.	μ_{∞} calc. (equation 1) from	$v =$	200.	400.	800.	1600.
NEt ₄ I.	$\mu_{400} = 47.8$	$\left\{ \begin{array}{l} \mu_{\infty} \text{ calc.} \\ \mu_{\infty} \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 42.2 \\ 41.6 \end{array} \right.$	$\left\{ \begin{array}{l} 43.4 \\ 43.4 \end{array} \right.$	$\left\{ \begin{array}{l} 44.3 \\ 45.0 \end{array} \right.$	$\left\{ \begin{array}{l} 45.0 \\ 45.8 \end{array} \right.$

3. *Acids.*

TABLE X.

Solvent: Thioacetic acid. T=0°. D=17.3.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	320.	640.	1280.
NEt ₄ I.	$\lambda_{440} = 52.5$	$\left\{ \begin{array}{l} \lambda_{\infty} \text{ calc.} \\ \lambda_{\infty} \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 33.2 \\ 32.7 \end{array} \right.$	$\left\{ \begin{array}{l} 36.6 \\ 36.6 \end{array} \right.$	$\left\{ \begin{array}{l} 39.6 \\ 40.2 \end{array} \right.$

4. *Acid Anhydrides.*

The dielectric constant of citraconic anhydride is 39. The agreement in this case is perfect.

TABLE XI.

Solvent: Citraconic anhydride. T=25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	100.	200.	400.	800.
NEt ₄ I.	$\lambda_{200} = 24.9$	$\left\{ \begin{array}{l} \lambda_{\infty} \text{ calc.} \\ \lambda_{\infty} \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 18.5 \\ 18.5 \end{array} \right.$	$\left\{ \begin{array}{l} 19.7 \\ 19.7 \end{array} \right.$	$\left\{ \begin{array}{l} 20.7 \\ 20.6 \end{array} \right.$	$\left\{ \begin{array}{l} 21.5 \\ 21.1 \end{array} \right.$

5. *Acid Chlorides and Bromides.*

In these solvents the agreement between the observed and calculated values of equivalent conductivity is always within the limits of experimental error, which is somewhat large.

6. *Esters.*

(a) *Organic Esters.*—The dielectric constant of methyl cyanoacetate is 28, and that of the ethyl ester is 26.

(b) *Inorganic Esters.*—Walden's data on the equivalent con-

ductivities of solutions of tetraethylammonium iodide in methyl sulphate, ethyl sulphate, and trimethyl borate are the most trustworthy. The dielectric constants are 46, 38, and 8 respectively. The agreement is always very good.

TABLE XII.

Solute: Tetraethylammonium iodide. $T=25^{\circ}$.

Solvent.	λ_{∞}	calc. (equation 2) from	$V' =$	100.	200.	500.	1000.	2000.
Methyl cyano- acetate.		$\lambda_{100} = 30.8$	$\left\{ \begin{array}{l} \lambda_{\infty} \text{ calc.} \\ \lambda_{\infty} \text{ obs.} \end{array} \right.$	$\begin{array}{l} 20.4 \\ 20.3 \end{array}$	$\begin{array}{l} 22.2 \\ 22.1 \end{array}$	$\begin{array}{l} 24.3 \\ 24.2 \end{array}$	$\begin{array}{l} 25.3 \\ 25.3 \end{array}$	$\begin{array}{l} 26.4 \\ 26.1 \end{array}$
Ethyl cyano- acetate		$\lambda_{100} = 28.1$	$\left\{ \begin{array}{l} \lambda_{\infty} \text{ calc.} \\ \lambda_{\infty} \text{ obs.} \end{array} \right.$	$\begin{array}{l} 17.9 \\ 17.7 \end{array}$	$\begin{array}{l} 19.7 \\ 19.6 \end{array}$	$\begin{array}{l} 21.6 \\ 21.6 \end{array}$	$\begin{array}{l} 22.8 \\ 22.8 \end{array}$	$\begin{array}{l} 23.8 \\ 23.6 \end{array}$

TABLE XIII.

Solvent: Methyl sulphate. $T=25^{\circ}$

Solute.	λ_{∞}	calc. (equation 2) from	$V' =$	200.	400.	800.	1600.	3200.
NEt ₄ I.		$\lambda_{100} = 44.3$	$\left\{ \begin{array}{l} \lambda_{\infty} \text{ calc.} \\ \lambda_{\infty} \text{ obs.} \end{array} \right.$	$\begin{array}{l} 36.1 \\ 35.5 \end{array}$	$\begin{array}{l} 37.7 \\ 37.7 \end{array}$	$\begin{array}{l} 38.9 \\ 38.7 \end{array}$	$\begin{array}{l} 39.9 \\ 39.6 \end{array}$	$\begin{array}{l} 40.7 \\ 40.4 \end{array}$

TABLE XIV.

Solvent: Ethyl sulphate. $T=25^{\circ}$.

Solute.	λ_{∞}	calc. (equation 2) from	$V' =$	200.	400.	800.	1600.
NEt ₄ I.		$\lambda_{100} = 40.5$	$\left\{ \begin{array}{l} \lambda_{\infty} \text{ calc.} \\ \lambda_{\infty} \text{ obs.} \end{array} \right.$	$\begin{array}{l} 31.9 \\ 30.3 \end{array}$	$\begin{array}{l} 33.5 \\ 33.5 \end{array}$	$\begin{array}{l} 34.9 \\ 35.6 \end{array}$	$\begin{array}{l} 36.0 \\ 36.7 \end{array}$

TABLE XV.

Solvent: Trimethyl borate. $T=25^{\circ}$.

Solute.	λ_{∞}	calc. (equation 2) from	$V' =$	200.	400.	800.
NEt ₄ I.		$\lambda_{100} = 32.5$	$\left\{ \begin{array}{l} \lambda_{\infty} \text{ calc.} \\ \lambda_{\infty} \text{ obs.} \end{array} \right.$	$\begin{array}{l} 10.2 \\ 10.2 \end{array}$	$\begin{array}{l} 13.0 \\ 13.0 \end{array}$	$\begin{array}{l} 15.7 \\ 16.5 \end{array}$

7. Amides, Amines, etc.

Among amides, formamide is a solvent that most resembles water. The inorganic salts dissolve in it quite as readily as in water, and, like the latter, it has a high dielectric constant, namely, 84.

Pyridine.—Laszczynski and Gorski have determined the conductivity of potassium iodide in pyridine solutions (*Zeitsch. Elektro-*

chem., 1897, 4, 290), whilst Walden has determined the equivalent conductivity of tetraethylammonium iodide at various dilutions (*Zeitsch. physikal. Chem.*, 1906, 55, 334). According to Schlundt, the dielectric constant of pyridine is 12.4 (*J. Physical Chem.*, 1901, 5, 157, 503).

TABLE XVI.

Solvent: Formamide. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	100.	200.	400.	800.
NEt ₄ I.	$\lambda_{298} = 29.0$	$\left\{ \begin{array}{l} \lambda_r \text{ calc.} \\ \lambda_r \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 25.2 \\ 25.0 \end{array} \right.$	$\left\{ \begin{array}{l} 26.0 \\ 26.0 \end{array} \right.$	$\left\{ \begin{array}{l} 26.5 \\ 26.6 \end{array} \right.$	$\left\{ \begin{array}{l} 27.0 \\ 27.2 \end{array} \right.$

TABLE XVII.

Solvent: Pyridine. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	100.	200.	400.	800.
NEt ₄ I.	$\lambda_{298} = 71.0$	$\left\{ \begin{array}{l} \lambda_r \text{ calc.} \\ \lambda_r \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 26.9 \\ 27.0 \end{array} \right.$	$\left\{ \begin{array}{l} 32.9 \\ 33.0 \end{array} \right.$	$\left\{ \begin{array}{l} 39.5 \\ 39.5 \end{array} \right.$	$\left\{ \begin{array}{l} 43.7 \\ 46.0 \end{array} \right.$

	λ_{∞} calc. (equation 2) from	$V' =$	178.5.	357.0.	714.0.
KI.	$\lambda_{214} = 50.0$	$\left\{ \begin{array}{l} \lambda_r \text{ calc.} \\ \lambda_r \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 22.8 \\ 22.0 \end{array} \right.$	$\left\{ \begin{array}{l} 26.9 \\ 26.2 \end{array} \right.$	$\left\{ \begin{array}{l} 30.7 \\ 30.7 \end{array} \right.$

8. Nitriles.

The nitriles are excellent ionisers, and their dielectric constants are high. Thus glycollonitrile has a dielectric constant as high as 68, whilst the dielectric constants of acetonitrile, propionitrile, and benzonitrile are 37, 27, and 26 respectively.

TABLE XVIII.

Solvent: Acetonitrile. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	200.	500.	1000.	2000.	4000.	8000.
NaI.	$\lambda_{300} = 190.3$	$\left\{ \begin{array}{l} \lambda_r \text{ calc.} \\ \lambda_r \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 155.0 \\ 151.0 \end{array} \right.$	$\left\{ \begin{array}{l} 165.9 \\ 165.9 \end{array} \right.$	$\left\{ \begin{array}{l} 172.3 \\ 171.0 \end{array} \right.$	$\left\{ \begin{array}{l} 177.4 \\ 176.7 \end{array} \right.$	$\left\{ \begin{array}{l} 182.0 \\ 181.0 \end{array} \right.$	$\left\{ \begin{array}{l} 1854 \\ 1833 \end{array} \right.$

TABLE XIX.

Solvent: Propionitrile. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	64.	128.	256.	512.	1024.
NEt ₄ I.	$\lambda_{128} = 169$	$\left\{ \begin{array}{l} \lambda_r \text{ calc.} \\ \lambda_r \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 102.6 \\ 102.0 \end{array} \right.$	$\left\{ \begin{array}{l} 113.7 \\ 113.7 \end{array} \right.$	$\left\{ \begin{array}{l} 123.5 \\ 123.4 \end{array} \right.$	$\left\{ \begin{array}{l} 131.6 \\ 131.5 \end{array} \right.$	$\left\{ \begin{array}{l} 138.6 \\ 138.4 \end{array} \right.$

TABLE XX.

Solvent: Benzonitrile. $T = 25^\circ$.

Solute.	λ_α calc. (equation 2)	$V' =$				
	from	200.	400.	800.	1600.	
NEt ₄ I.	$\lambda_{100} = 55.6$	λ_α calc.	39.0	42.0	44.5	46.6
		λ_α obs.	37.7	42.0	45.0	47.6

TABLE XXI.

Solvent: Glycollonitrile. $T = 25^\circ$.

Solute.	λ_α calc. (equation 2)	$V' =$		
	from	100.	200.	800.
NEt ₄ I.	$\lambda_{200} = 79.5$	λ_α calc.	67.0	69.4
		λ_α obs.	66.8	69.4

TABLE XXII.

Solvent: Acetonitrile. $T = 25^\circ$.

Solute.	μ_α calc. (equation 2)	$v =$		
	from	100.	200.	400.
CuBr ₂	$\mu_{200} = 73.9$	μ_α calc.	49.8	54.0
		μ_α obs.	48.6	54.0

9, 10. *Thiocyanates and Thiocarbimides.*

The calculated values of equivalent conductivity also agree well with Walden's data for these solvents.

11, 12. *Nitro-compounds and Dimethylnitrosoamine.*

The dielectric constants of nitromethane and dimethylnitrosoamine are 39 and 53.3 respectively.

TABLE XXIII.

Solvent: Nitromethane. $T = 25^\circ$.

Solute.	λ_α calc. (equation 2)	$V' =$				
	from	100.	200.	400.	800.	1600.
NEt ₄ I.	$\lambda_{200} = 127.8$	λ_α calc.	94.5	100.5	105.4	109.6
		λ_α obs.	94.0	100.5	105.9	112.0

TABLE XXIV.

Solvent: Dimethylnitrosoamine. $T = 25^\circ$.

Solute.	λ_α calc. (equation 2)	$V' =$			
	from	250.	500.	1000.	2000.
NEt ₄ I.	$\lambda_{500} = 92.0$	λ_α calc.	78.3	81.2	83.2
		λ_α obs.	77.5	81.2	84.2

C C⁶

13. *Ketones.*

The dielectric constant of acetone is 21, and that of acetylacetone is 22 at 25°.

TABLE XXV.

Solvent: Acetone. T=25°.

Solute.	μ_{∞} calc. (equation 1) from	$v =$	256.	512.	1024.
NaI	$\mu_{111} = 158.5$	$\left\{ \begin{array}{l} \mu_{\infty} \text{ calc.} \\ \mu_{\infty} \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 127.0 \\ 126.3 \end{array} \right.$	$\left\{ \begin{array}{l} 133.0 \\ 133.0 \end{array} \right.$	$\left\{ \begin{array}{l} 138.0 \\ 139.0 \end{array} \right.$

TABLE XXVI.

Solvent: Acetylacetone. T=25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	200.	400.	800.	1600.
NEt ₄ I.	$\lambda_{100} = 86.4$	$\left\{ \begin{array}{l} \lambda_{\infty} \text{ calc.} \\ \lambda_{\infty} \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 56.9 \\ 56.7 \end{array} \right.$	$\left\{ \begin{array}{l} 62.0 \\ 62.0 \end{array} \right.$	$\left\{ \begin{array}{l} 68.4 \\ 65.5 \end{array} \right.$	$\left\{ \begin{array}{l} 70.0 \\ 68.7 \end{array} \right.$

14. *Epichlorohydrin.*

TABLE XXVII.

Solvent: *epi*Chlorohydrin. T=25°. D=26.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	100.	200.	400.	800.	1600.
NEt ₄ I.	$\lambda_{100} = 63.7$	$\left\{ \begin{array}{l} \lambda_{\infty} \text{ calc.} \\ \lambda_{\infty} \text{ obs.} \end{array} \right.$	$\left\{ \begin{array}{l} 42.1 \\ 40.0 \end{array} \right.$	$\left\{ \begin{array}{l} 46.0 \\ 45.0 \end{array} \right.$	$\left\{ \begin{array}{l} 49.6 \\ 49.6 \end{array} \right.$	$\left\{ \begin{array}{l} 52.6 \\ 53.7 \end{array} \right.$	$\left\{ \begin{array}{l} 55.1 \\ 56.6 \end{array} \right.$

Conclusion.

It will be seen that equations 1 and 2 have been subjected to a very severe test, and that their validity has been completely confirmed by the mass of experimental data on the conductivity of salt solutions in some thirty solvents.

The term "degree of dissociation" thus loses all significance in the case of strong electrolytes. In his first paper on the conduction of electricity by electrolytes, Arrhenius (*Bihang. der. Stockholmer. Akad.*, 1883, 8, Nos. 13, 14) used the term "activity coefficient" for the ratio μ_v/μ_{∞} , and this is, indeed, a very suitable term in view of the fact successfully demonstrated here, that in salt solutions there are only free and bound ions. Incidentally, there has also been obtained a valuable method of determining the mode of dissociation of a solute in any solvent. Walden's normal electrolyte, tetraethylammonium iodide, really dissociates

abnormally. It is, however, the peculiar characteristic of this solute that the same type of dissociation persists in all the solvents. To this property are due the many regularities that Walden observed in tetraethylammonium iodide solutions. Thus we have his empirical law that "if solutions of one and the same normal electrolyte, tetraethylammonium iodide, in various solvents have the same degree of dissociation (activity coefficient), then for all solvents, the product of the dielectric constant, and the cube root of the dilution of that solution has always a constant value. Thus $D\sqrt[3]{V} = D'\sqrt[3]{V'}$, etc. = k , where D , D' , etc., are the dielectric constants of the solvents, and V , V' , etc., are the respective dilutions at which the activity-coefficient of tetraethylammonium iodide is the same. The theoretical significance of this general empirical law is at once brought out by equation 2. Since the mode of dissociation of the salt is always the same, the equation:

$$\frac{3N \cdot E^2 \cdot 2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{3 \sqrt[3]{V}}} = 3RT \log \frac{\mu_\infty}{\mu_0}$$

is applicable to its solution in all solvents. For the same value of μ_0/μ_∞ it is obvious that

$$D \sqrt[3]{V} = k,$$

whatever be the nature of the solvent.

It was rightly suggested by Nernst and Thomson that the dielectric constant is the fundamental property which determines the dissociating power of a solvent. Walden's investigations proved conclusively that a direct parallelism exists between the dissociating power and the dielectric constants of solvents. The idea, however, never passed beyond the qualitative stage. In this paper, in the author's opinion, it has been proved beyond doubt that the exact quantitative relation between the activity-coefficient and the dielectric constant is given by equations 1 and 2.

Finally, it should be pointed out that the fundamental problem to be solved in this connexion is the work necessary to separate the constituent ions of a gram-molecule of a salt to an infinite distance at a given dilution. The assumption that the ions of a binary electrolyte are arranged according to a simple cubic lattice is necessarily arbitrary, although it is the simplest possible view. Some other views are possible, for example, we may have a face-centred cube lattice, a cube-centred lattice, etc. For ternary electrolytes good results have been obtained by assuming an arrangement corresponding with a fluor spar lattice. Here, also, it is possible that an ion, instead of occupying the centre of a cube, may be displaced diagonally towards an oppositely charged ion or towards an empty corner. Bragg has actually observed such dis-

placement in crystals of iron pyrites. It is therefore not necessary that the above rigid forms of equation should always be applicable. It ought to be always possible, however, to express the relation between the activity-coefficient, the dilution, and the dielectric constant of the solvent by equations of the above type. The behaviour of acetone solutions of ammonium iodide is a case in point. Equation 2 does not hold good in this case. If, however, we assume that the NH_4^+ ions are displaced diagonally towards the oppositely charged I_2^{2-} ion by one-fourth the length of the diagonal we get the following equation:

$$\frac{3N \cdot E^2 \cdot 4 \sqrt[3]{2N}}{D \cdot \sqrt[3]{3} \cdot \sqrt[3]{V}} = \frac{3RT \log_e \mu_\alpha}{\mu_v}$$

which holds good exactly as shown in table XXVIII.

TABLE XXVIII.

Solvent: Acetone.

Solute.	λ_∞ calc. from	$V' =$	128.	256.	512.	1024.	2048.
NH_4I .	$\lambda_{512} = 209$	λ_v calc.	69.0	86.9	104.1	120.2	135.0
		λ_v obs.	67.5	85.5	104.1	120.8	136.0

The above theory should not, therefore, be rejected in those cases where equations 1 and 2 do not hold good. We should rather proceed in the reverse direction, that is, calculate the total potential energy of the electrical doublets at a given dilution, from the observed value of the activity-coefficient at that dilution. An insight into the arrangement of ions in the interior of a solution will then be easily obtained, and the next problem will be to determine whether the equation based on this particular arrangement holds good at other dilutions. Theory demands that such should be the case, and it fails if the observed and the calculated activity-coefficients do not agree. In some cases, however, chemical action may interfere, as in the hydrolysis of salts, and these should be regarded as abnormal.

The fundamental hypothesis that only ions exist in salt solutions requires no elaborate justification in view of the fact conclusively established that even in a salt crystal there is no such thing as a molecule.

My best thanks are due to Prof. P. C. Rây, and to my friend and colleague, Mr. J. N. Mukherjee.

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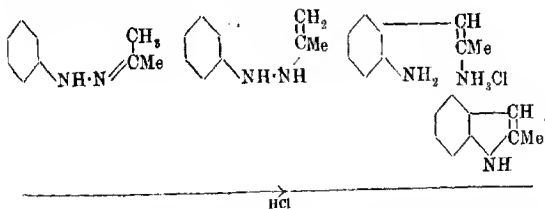
LIV.—A New Synthesis of Tetraphenylpyrrole.

By GERTRUDE MAUD ROBINSON and ROBERT ROBINSON.

IN the course of an investigation having for its object the preparation of pyrrole, as a starting point for tropine, by an improved method, our attention was naturally directed to known methods of producing the pyrrole nucleus, among which E. Fischer's well-known synthesis of indole derivatives (*Annalen*, 1886, **236**, 126) occupies a prominent position. A necessary preliminary, however, to an attempt to apply an analogous process to the formation of true pyrroles seemed to be the formulation of a clear idea of the mechanism of the reactions involved in the decomposition of phenylhydrazones, and we have adopted a hypothesis which includes the following three stages:

- (1) The transformation of the hydrazone into an unsaturated hydrazine, which is the isomeric change of an eninic into an enamic modification (compare J. F. Thorpe, P., 1909, **25**, 309). This is assumed to occur by the addition of the acid reagent and decomposition of the additive product.
- (2) The benzidine-type rearrangement of the resulting hydrazine.
- (3) Ring-formation by elimination of ammonium salt from the product, analogous to the formation of piperidine from the hydrochloride of pentamethylenediamine.

These changes are represented below in the case of the synthesis of 2-methylindole from the phenylhydrazone of acetone.



It will at once be recognised that the conditions necessary for the reaction, namely, an acid reagent and an elevated temperature, are those which would be expected to favour each of the above stages if considered separately, and in accordance with experience of molecular transformations due to the intervention of an acidic reagent it is noted that each stage is more basic than the last until, finally, the basic character is neutralised by the accident of

the formation of a ring of benzenoid character.* Thus a hydrazine is more basic than a hydrazone, and the hypothetical diamino-compound should be more basic still.

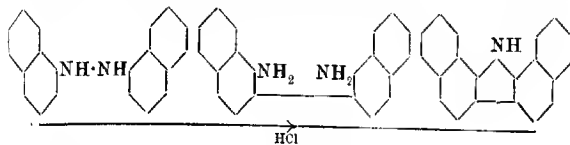
It seems probable that there is analogy between the enimic to enamic transformation and the ketone to enol change, and that the former would be likely to occur more easily in the cases of the hydrazones of those ketones which are readily changed to enols or enolic derivatives. The aldehydes and ketones, which are readily changed to enols, might therefore be expected to give phenylhydrazones readily convertible to indole derivatives if our hypothesis can be upheld. This is in accordance with experimental results, as the following examples show. Semmler (*Ber.*, 1909, **42**, 584) found that phenylacetaldehyde was converted into the acetate of the enolic modification by boiling with acetic anhydride, whereas acetophenone shows no such behaviour. Now Fischer and Schmitt (*Ber.*, 1888, **21**, 1072) showed that phenylacetaldehyde-phenylhydrazone was extremely easily transformed to phenylindole, and even by boiling with an alcoholic solution containing one-fifth of a molecular proportion of hydrochloric acid. On the other hand, acetophenonephenylhydrazone required heating with zinc chloride at 180° (Fischer, *loc. cit.*, p. 133). A similar comparison may be made between the cyclic ketones, such as cyclohexanone and corresponding open-chain ketones. The former are well known to be more reactive than the latter in reactions which are assumed to depend on the enolic modification of the substances, and again the phenylhydrazones of the cyclic ketones are more readily transformed into indole derivatives than is the case with the phenylhydrazones of such ketones as diethyl ketone (compare Baeyer, *Annalen*, 1893, **278**, 106; Plancher, *Gazzetta*, 1898, **28**, ii, 387; Mannich, *Ber.*, 1906, **39**, 1594). In general, indoles appear to be readily produced from the phenylhydrazones of aldehydes and ketones which contain a negative group, particularly when this is in the β -position with respect to the carbonyl group.

It is interesting that Nef (*Annalen*, 1891, **266**, 71) observed the production of an indole derivative by dissolving ethyl β -phenylhydrazinocrotonate in concentrated sulphuric acid. This condensation product of phenylhydrazine and ethyl acetoacetate has

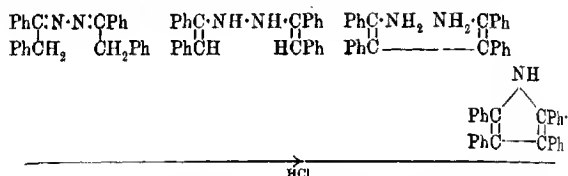
* The complete cyclic conjugation, which is probably the most characteristic feature of systems recognised as benzenoid, demands in the case of pyrrole a call on the latent valencies of the nitrogen atom. In pyridine, however, the latent valencies remain unaltered. It is possible, therefore, that a salt of pyridine retains its aromatic nucleus, whereas a salt of pyrrole cannot do so. Further, the latent valencies in pyrrole having been weakened, the preliminary dissociation necessary before salt-formation can take place is less likely to occur.

undoubtedly the unsaturated hydrazine structure, since it may be oxidised by mercuric oxide to an azo-compound previously obtained by Bender (*Ber.*, 1887, **26**, 2747), but under most conditions of condensation it merely loses alcohol with the formation of phenylmethylpyrazolone.

In the second phase of the reaction, an ortho-benzidine-type rearrangement has been assumed, and this may be realised in the case of certain naphthalene derivatives. Thus Nietzki and Goll (*Ber.*, 1885, **18**, 3252) obtained the isomeric diaminodinaphthyls, naphthidine and dinapbthylene, by the action of stannous chloride and hydrochloric acid on α -azonaphthalene, and, further, obtained a dinaphthacarbazole by boiling dinapbthylene with concentrated hydrochloric acid. Vesely (*Ber.*, 1905, **38**, 136) determined the constitution of the dinapbthacarbazole by an independent synthesis, so that the following changes are established:



seemed to be that divinylhydrazine and its derivatives should be convertible by acids into pyrrole and substituted pyrroles. Continuing this line of argument and reasoning from the first stage assumed above, it appeared not improbable that azines of substances containing the group $\cdot\text{CH}_2\cdot\text{CO}\cdot$ might also, under correct conditions, be transformed into pyrroles. In this case, the initial tautomeric change is a double one and only likely to occur with facility in the molecules of azines of those ketones or aldehydes which show a marked tendency to change to related enols. To test our hypothesis, we chose what was regarded as one of the more favourable cases, namely, that of the azine of deoxybenzoin, and found that the action of dry hydrogen chloride on this substance at 180° converted it in almost a quantitative manner into the expected tetraphenylpyrrole and ammonium chloride. The reactions involved are represented below, in accordance with the views already discussed.



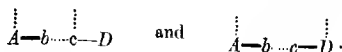
The scope of the reaction has not yet been defined, but in the case of the simpler aliphatic azines there is the competing transformation to pyrazolines, and we have been unable to obtain pyrrole from acetaldazine or dimethylpyrrole from dimethyl ketazine. The above explanation assumes what is perhaps a somewhat wider view of the benzidine transformation than is generally held, and in this connexion we have found the theory of partial dissociations serviceable.

The following brief statement expresses the form in which this and related reactions may be generalised. In a molecular complex $\text{A} \cdots \text{b} \cdots \text{c} \cdots \text{D}$, *b* or *c* or both represent atoms capable of assuming a higher valency by salt-formation. The salt absorbs energy and

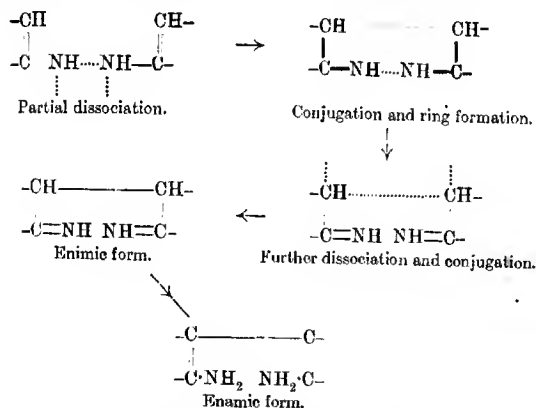
passes into an activated condition,* represented by $\text{A} \cdots \text{b} \cdots \text{c} \cdots \text{D}$

* The activated molecules are said to be 'partially dissociated' because the phenomenon appears to be a stage towards complete ionic dissociation, but the physical basis of the process is not quite clear. It may be that the energy change causes the movement of an electron from one atom to another (polarisation of the molecule) or a mere change in the position of one or more electrons within the sphere of the atom itself. In this case the evidence shows that the change is repeated in the same sense in alternate atoms

omitting the acid for reasons of convenience. If the partial valencies become conjugated with unsaturated groups in *A* or *D*, we obtain



Ring-formation by the partial valencies followed by a second similar complete process leads in the first case to $b-A-c-D$ and in the second to $b-A-D-c$. The products are obtained in the *keto*-, *enimic*, or *thioketo*-modifications, according as the atoms *b* or *c* are oxygen, nitrogen, or sulphur. The less extensive change is represented by the semidine transformation, the conversion of phenylhydrazine into *p*-phenylenediamine, of phenylnitroamine into nitroaniline, and by many other reactions. The full change resulting from conjugation of the partial valencies with both unsaturated groups *A* and *D* is represented by the benzidine rearrangement, and it is obvious that even within the four corners of the general scheme the nature of the products may be considerably varied according as the conjugated chains in *A* and *D* are long or short. The type of rearrangement assumed to occur in the synthesis of indole derivatives is represented below, and the thickened lines stand for a normal valency plus a partial valency.



forming part of a conjugated chain and in the opposite sense in the other atoms of the chain. Several further suggestions might be made, especially that a part use may be made of the field surrounding a single electron.

EXPERIMENTAL.

Preparation of Azines.

The processes described in the literature for the preparation of azines, and especially the ketazines, are far from convenient, and the employment of free hydrazine does not, in our experience, give such good results as that of a hydrazine salt and sodium acetate. The ketazines are readily obtained by the interaction of the calculated amounts of ketone and hydrazine sulphate in boiling aqueous alcohol in the presence of excess of sodium acetate. The yields correspond closely with those demanded by theory.

Phenyl benzyl ketazine was prepared by boiling a mixture of deoxybenzoin (6.3 grams), hydrazine sulphate (2.2 grams), sodium acetate (7 grams), water (60 c.c.), and alcohol (125 c.c.) during two hours under reflux. The product was collected and crystallised from ethyl acetate, and then melted at 164° , as stated by Curtius and Blumer (*J. pr. Chem.*, 1895, [ii], 52, 137). This azine is quickly and completely hydrolysed by heating for a minute with alcohol and hydrochloric acid, and on the addition of water pure deoxybenzoin is precipitated. In view of the sparing solubility of the derivative, it may advantageously be employed for the otherwise rather troublesome purification of crude deoxybenzoin.

Tetraphenylpyrrole.

Evidence of the formation of tetraphenylpyrrole was obtained when phenyl benzyl ketazine was heated with zinc chloride, but the yield is much improved when dry hydrogen chloride is passed over the melted substance contained in a vessel heated at 180° in an oil-bath. The reaction was prolonged during an hour, and the solid product was found to consist of a mixture of ammonium chloride and the pyrrole derivative. The mass was extracted with sufficient hot acetic acid, and the crystals which separated on cooling were collected and washed with a little water to remove traces of ammonium salt. The yield of crude, dry tetraphenylpyrrole amounted to 88 per cent. of the theoretical. The substance was recrystallised several times from acetic acid, and obtained in colourless, flat needles melting at $214-215^{\circ}$. A specimen was prepared according to Garrett's method (*Ber.*, 1888, 21, 3107), and found to melt at $214-215^{\circ}$, and a mixture of the two also melted at the same temperature.

The yellow solution in sulphuric acid becomes ivy-green on the addition of a trace of a nitrite or of a drop of nitric acid. In the

latter case, however, the liquid soon becomes brown, and on the addition of water a yellow nitro-derivative is precipitated. Acetaldazine and dimethyl ketazine were submitted to the action of dry hydrogen chloride, sulphanilic acid, and a number of other acid reagents and salts, such as zinc chloride, under varied conditions, but in all cases no pyrrole derivative was obtained, the only products being the corresponding pyrazoles and pyrazolines.

The formation of benzidine from hydrazobenzene has been discussed above, and a theory which has been occasionally advocated regards the transformation as passing through the intermediate stage of *p*-aminodiphenylamine. The method of preparation of this substance indicates its stability under conditions which favour the transformation of hydrazobenzene into benzidine, but to be more sure we prepared the compound by the usual process and endeavoured to convert it into benzidine, but without success. It was entirely unaffected by boiling with dilute or concentrated hydrochloric acid. 0.9 Gram of aminodiphenylamine was boiled during thirty minutes with 15 c.c. of concentrated hydrochloric acid; 0.82 gram of unaltered substance melting, after crystallisation from light petroleum, at 66–67° was recovered.

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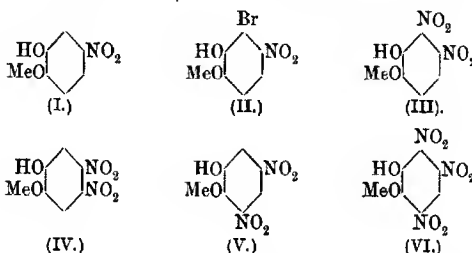
L.V.—Nitro-derivatives of Guaiacol.

By FANNY POLLECOFF and ROBERT ROBINSON.

THE opinion has been expressed (Jones and Robinson, T., 1917, 111, 906*) that negative groups in the meta-position with respect

* In this paper the melting point of 6-bromoacetoveratrylamide was wrongly given owing to a clerical error (*loc. cit.*, p. 913). The melting point of this substance is 127°. In the same communication 6-nitroacetoveratrylamide melting at 199° and 6-nitroveratrylamine melting at 175° were described. Simonsen and Rau (this vol., p. 28) prepared the same substances and assigned to them the respective melting points 196° and 171°. A redetermination of the melting points of the specimens which had been preserved gave 199° for the acetyl derivative, whilst 6-nitroveratrylamine melted at 174.5°. The latter crystallises both in needles and in prisms. It is possible that the discrepancy is due to the fact that Jones and Robinson nitrated acetoveratrylamide in acetic acid solution, whilst Simonsen and Rau employed more concentrated nitric acid (D 1.4). Simonsen and Rau (*loc. cit.*) experienced difficulty in preparing veratrylamine unmixed with its chloro-derivative by the reduction of nitroveratrole with tin and hydrochloric acid, but were finally able to obtain a 50 per cent. yield by reducing at 100° with tin and hydrochloric acid in presence of graphite. We found that an

to a positive group exert an influence which is in the direction of favouring ortho-substitution with respect to the positive orientator. An example was found in the bromination of 5-nitroguaiacol (I), which yielded 6-bromo-5-nitroguaiacol (II), and we have now investigated the nitration of the same substance, and find that the main product is 5:6-dinitroguaiacol (III), mixed, however, with no inconsiderable proportion of 4:5-dinitroguaiacol (IV).



It was obviously interesting to extend the inquiry to the nitration of 3:5-dinitroguaiacol (V), in which there are two negative groups in the meta-position with respect to the phenolic hydroxyl. The desired substance was obtained by the nitration of guaiacol carbonate, which was changed first to a dinitro-derivative, the carbonate of 5-nitroguaiacol, and then to a tetranitro-derivative, which on hydrolysis yielded the new 3:5-dinitroguaiacol.

As was anticipated, the nitration of the latter resulted in 3:5:6-trinitroguaiacol (VI) as the sole product. The necessary proofs of constitution are obtained from the observations that the dinitroguaiacol from the tetranitro-derivative of guaiacol carbonate yields 4:6-dinitroveratrole on methylation, and that the methyl ether of the trinitroguaiacol is a new trinitroveratrole melting at 174°. The melting points of the known nitroguaiacols are tabulated below, in order to bring out the striking divergences which exist:

4-Nitroguaiacol, 101—102°.

5-Nitroguaiacol, 105°

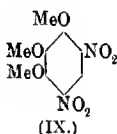
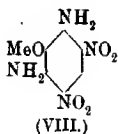
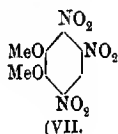
6-Nitroguaiacol, 62°.

excellent yield could be obtained by shaking the nitroveratrole with tin, stannous chloride, hydrochloric acid, and some acetic acid in the cold until the reaction was complete. The amine was usually isolated as the acetyl derivative by eliminating the tin by the addition of zinc, and after rendering strongly alkaline with sodium hydroxide the solution was agitated with acetic anhydride. The crystalline precipitate of acetoveratrylamide was collected. Further quantities could be obtained by extraction of the alkaline solution with ether.

R. E.

- 3-Nitroguaiacol is unknown.
 3:5-Dinitroguaiacol, 80°.
 3:6-Trinitroguaiacol, 129° (decomp.) 3:4:5-, 4:5:6-, and 3:4:6-trinitroguaiacols are unknown.
 4:6-Dinitroguaiacol, 124°.
 4:5-Dinitroguaiacol, 172°.
 5:6-Dinitroguaiacol, 205—208° (decomp.).
 3:5- and 3:4-Dinitroguaiacols are unknown.

3:5:6-Trinitroveratrole (VII) is changed by aqueous methyl-alcoholic ammonia into 3:5-dinitro-2:6-diaminoanisole (VIII), and by methyl-alcoholic sodium hydroxide into 4:6-dinitro-1:2:3-trimethoxybenzene (IX). The nitro-group displaced by ammonia is therefore that which is also displaceable by methoxyl, and in this respect the substance differs from the isomeric 3:4:5-trinitroveratrole, in which the nitro-group in position 4 is affected by ammonia, whilst that in position 5 is displaced by methoxyl when the trinitroveratrole is heated with a solution containing sodium methoxide.



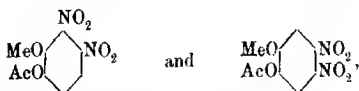
EXPERIMENTAL.

Preparation of 4-Nitroguaiacol.

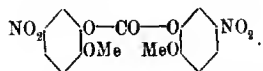
Cardwell and Robinson (T., 1915, **107**, 255) prepared this substance by the hydrolysis of nitroveratrole by means of boiling aqueous methyl-alcoholic potassium hydroxide, but the yield was not quite satisfactory, and a certain amount of neutral material was recovered. It is now found that this consists partly of azoxyveratrole (compare G. M. Robinson, T., 1917, **111**, 109), and that if the methyl alcohol is omitted, the hydrolysis, although slow, proceeds practically quantitatively. The modified process constitutes by far the most convenient method available for the preparation of 4-nitroguaiacol. Nitroveratrole (5 grams) was boiled during thirty-six hours with a 10 per cent. aqueous solution (100 grams) of potassium hydroxide under reflux, and, on cooling, the potassium salt of the nitroguaiacol crystallised in golden-orange needles. Sufficient water to dissolve the salt was added, and on the addition of hydrochloric acid, 4-nitroguaiacol was precipitated in the crystalline condition, and was collected and dried in the air.

Nitration of 4-Nitroguaiacol and its Acetyl Derivative.

4-Nitroguaiacol was dissolved in nitric acid (D 1.42), when immediate reaction ensued, and, on the addition of water, a mass of needle-shaped crystals of 4:6-dinitroguaiacol was precipitated. The substance melted at 123° after crystallisation from alcohol, and gave a methyl ether melting after crystallisation at 101–102°. The yield closely approximated to that demanded by theory. 4-Nitroguaiacyl acetate is not affected by cold nitric acid (D 1.42), and although it is attacked by the fuming acid (D 1.5), the experiment is rather unsatisfactory, owing to the considerable loss which occurs through oxidation. The acetyl derivative was dissolved in ten times its weight of nitric acid (D 1.5), and the mixture cooled in running water at 15° during fifteen minutes. The product was poured into water, when the oil soon solidified, and after collection, washing, and drying, weighed approximately half as much as the material employed. Repeated crystallisations from methyl alcohol resulted in the isolation of unchanged 4-nitroguaiacyl acetate, but, after hydrolysing the acetyl derivatives contained in the mother liquors by the addition of dilute aqueous potassium hydroxide and gently heating the solution, a precipitate of 4:5-dinitroguaiacol (see below) was obtained on acidification. When the nitration was carried out during only two minutes, much unchanged material was recovered, and the methyl-alcoholic mother liquors were in this case treated with potassium hydroxide and methyl sulphate in large excess; the resulting methyl ethers on repeated crystallisation from methyl alcohol yielded pure 3:4-dinitroveratrole melting at 91°. The nitration of 4-nitroguaiacyl acetate, therefore, results in the production of the compounds



in undetermined proportions, and the loss on continued nitration appears to be due to the destruction of the first of these by oxidation.

5-Nitro-2-methoxyphenyl Carbonate,

Guaiacol carbonate (10 grams) was finely powdered and added in one portion to nitric acid (100 c.c., D 1.42), mechanically stirred,

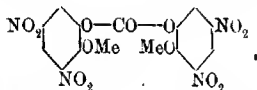
and cooled to 0° . These conditions were maintained during three hours; water was then added, and the nearly colourless product collected and well washed with water. The yield is excellent and the material sufficiently pure for further experiments, especially if it be extracted with a little warm alcohol. The substance crystallises from methyl alcohol in colourless needles melting at 133° , and moderately sparingly soluble in the usual solvents:

0.1663 gave 0.2999 CO_2 and 0.0510 H_2O . $\text{C} = 49.2$; $\text{H} = 3.4$.

$\text{C}_{16}\text{H}_{12}\text{O}_9\text{N}_2$ requires $\text{C} = 49.5$; $\text{H} = 3.3$ per cent.

The substance yields 5-nitroguaiacol on hydrolysis, and is a convenient source of the latter. The carbonate (4 grams) was heated on the steam-bath with a solution of sodium hydroxide (3 grams) in water (60 c.c.) until a clear solution was obtained on dilution with water. On acidification with hydrochloric acid, pure 5-nitroguaiacol was obtained in needles.

3:5-Dinitro-2-methoxyphenyl Carbonate,



The foregoing carbonate of 5-nitroguaiacol (3 grams) was dissolved in nitric acid (20 c.c., D 1.5), and the solution allowed to remain at the ordinary temperature during four hours. A certain proportion of the tetranitro-derivative separated in needles and the remainder was precipitated on the addition of water. The yield was almost that demanded by theory. The substance separated from benzene in short, colourless needles melting at 148° :

0.2113 gave 0.3050 CO_2 and 0.0403 H_2O . $\text{C} = 39.4$; $\text{H} = 2.1$.

$\text{C}_{15}\text{H}_{10}\text{O}_{13}\text{N}_4$ requires $\text{C} = 39.6$; $\text{H} = 2.2$ per cent.

This compound is readily soluble in ethyl acetate, sparingly so in ether or alcohol, and moderately so in benzene. There was no evidence of the formation of isomeric nitro-derivatives in the two stages of the nitration of guaiacol carbonate.

3:5-Dinitroguaiacol (V).

The carbonate (20 grams) described in the last section was heated on the steam-bath with sodium carbonate (50 c.c. of saturated aqueous solution), water (100 c.c.), and alcohol (30 c.c.) until a homogeneous solution resulted. After cooling, the nitrophenol was precipitated by the addition of hydrochloric acid, collected, washed

with water, and dried (18.5 grams). The substance was readily soluble in alcohol or ethyl acetate, more sparingly so in benzene, chloroform, or carbon disulphide. It was crystallised from toluene and then from carbon disulphide, and obtained in pale yellow needles melting at 80°:

0.2948 gave 0.4203 CO₂ and 0.0699 H₂O. C=39.0; H=2.6.

C₇H₆O₆N₂ requires C=39.2; H=2.8 per cent.

This dinitroguaiacol dissolves readily in aqueous sodium carbonate to a yellow solution, and the sodium salt is obtained in glistening, orange needles by the addition of sodium hydroxide. Not containing a nitro-group in the ortho- or para-position with respect to the hydroxyl group, this substance may be comparatively readily methylated in alcoholic solution by means of methyl sulphate and potassium hydroxide, but even in this case it was found more convenient to employ the xylene-methyl sulphate-sodium carbonate method. The methyl ether was identified with 3:5-(or 4:6)-dinitroveratrole, melting after crystallisation from alcohol at 102°.

5:6-Dinitroguaiacol (III).

5-Nitroguaiacol (15 grams) in acetic acid (50 c.c.) was nitrated by the addition of nitric acid (20 c.c., D 1.42), diluted with acetic acid (10 c.c.) with constant stirring, and cooling in running water. The first half of the acid mixture was added during five minutes and the second portion during one minute. Water was then added immediately, and the product collected, washed, and dried (14.7 grams). This was dissolved in hot ethyl acetate (65 c.c.), and, on cooling, 4.8 grams of well-defined yellow prisms were deposited. The mother liquor was mixed with an equal volume of benzene, and this induced no further separation, but, on the addition of 100 c.c. of light petroleum, 2.5 grams gradually crystallised. This material was a mixture, and by further treatment with ethyl acetate and light petroleum ultimately yielded 2.2 grams of the yellow prisms. A further 0.1 gram was obtained from the mother liquors after separation of the 4:5-isomeride (see below), so that the total yield was 7.1 grams. The substance so isolated was practically pure 5:6-dinitroguaiacol, and it was crystallised, first from ethyl acetate and then again from toluene, and obtained in pale yellow prisms which became orange at about 200° and began to melt at 205°, with vigorous decomposition near 208°:

0.1071 gave 0.1547 CO₂ and 0.0280 H₂O. C=39.4; H=2.9.

C₇H₆O₆N₂ requires C=39.2; H=2.8 per cent.

This substance is more sparingly soluble in most organic solvents

than any of the isomerides which we have examined. It dissolves in aqueous sodium carbonate, and, on the addition of concentrated sodium hydroxide, an orange salt is precipitated in shining needles.

The *acetyl* derivative is obtained by heating the nitrophenol with acetic anhydride, and crystallises from alcohol, in which it is somewhat sparingly soluble in the cold, in slender, pointed, colourless needles melting at 124–125°.

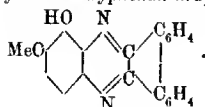
The *methyl ether* is identical with 3:4-dinitroveratrole, and was prepared by methylation with methyl sulphate and sodium carbonate in boiling xylene solution. The residue from the removal of the solvent in a current of steam was collected and crystallised many times from methyl alcohol, and obtained in flat needles melting at 91°:

0.1158 gave 0.1784 CO_2 and 0.0383 H_2O . $\text{C}=42.0$; $\text{H}=3.7$.

$\text{C}_8\text{H}_5\text{O}_6\text{N}_2$ requires $\text{C}=42.1$; $\text{H}=3.5$ per cent.

Jones and Robinson (T., 1917, 111, 911) obtained a product melting at 96°, with previous softening, by the nitration of 3-nitroveratrole, and this was shown to contain 3:4-dinitroveratrole, because, after reduction and condensation with phenanthraquinone, 1:2-dimethoxyphenanthraphenazine (Pisovschi, *Ber.*, 1910, 43, 2137) was obtained. It was pointed out at the time that the product was obviously impure, and it now appears that it must have contained 4:5-dinitroveratrole, owing to the presence of 4-nitroveratrole in the 3-nitroveratrole, which was the starting point, and we have therefore repeated the experiment with carefully purified 3-nitroveratrole, and have obtained a product melting at 91° and identical with that described above.

1-Hydroxy-2-methoxyphenanthraphenazine,



5:6-Dinitroguaiacol was reduced by the addition of zinc dust in excess to its solution in aqueous alcoholic hydrochloric acid, and the filtered solution, mixed with sodium acetate, was then heated with phenanthraquinone dissolved in hot aqueous sodium hydrogen sulphite. The precipitated phenazine derivative was collected and washed with alcohol, after which it was crystallised from acetic acid, and again by adding alcohol to its solution in nitrobenzene. It was obtained in glistening, golden-yellow needles melting at 224°, and dissolving in sulphuric acid to a rose-red solution:

0.0961 gave 0.2715 CO_2 and 0.0418 H_2O . $\text{C}=77.5$; $\text{H}=4.7$.
 $\text{C}_{21}\text{H}_{14}\text{O}_2\text{N}_2$ requires $\text{C}=77.3$; $\text{H}=4.3$ per cent.

In alcoholic suspension, the substance was converted by sodium hydroxide into a dull mauve-red sodium salt, which reacted very readily with methyl sulphate with the production of 1:2-dimethoxyphenanthraphenazine (Pisovschi, *loc. cit.*), melting after crystallisation from alcohol at 175° . The curious colour of this sodium derivative appeared to be characteristic of the substance, and persists in the microscopic threads which separate from hot alcoholic solutions of the compound.

4:5-Dinitroguaiacol (IV).

The ethyl acetate-benzene-light petroleum mother liquor from the crystallisation of 5:6-dinitroguaiacol in the preparation described above (starting with 15 grams of 5-nitroguaiacol) was shaken with dilute sodium hydroxide, and the separated aqueous solution acidified with hydrochloric acid. The recovered nitrophenols were collected and found to consist chiefly of 4:5-dinitroguaiacol. The material was crystallised from a litre of boiling water, and obtained in long, yellow needles, and then again from toluene. The aqueous mother liquor was rendered alkaline and used to wash the toluene mother liquors, after which the solution was acidified and extracted with ether. The residue, after evaporation, was submitted to treatment with ethyl acetate, and, as already stated, some 5:6-dinitroguaiacol was isolated. Altogether, 5.7 grams of the 4:5-isomeride were obtained. The substance crystallised in long, pale yellow needles melting, when quite pure, at 172° , but many crystallisations are necessary in order to reach this value, and apparently pure material melted at $163\text{--}165^\circ$. The purest specimen was obtained by crystallisation from water followed by recrystallisation from alcohol and from xylene:

0.1439 gave 0.2045 CO_2 and 0.0350 H_2O . $\text{C}=38.8$; $\text{H}=2.8$.
 $\text{C}_7\text{H}_6\text{O}_6\text{N}_2$ requires $\text{C}=39.2$; $\text{H}=2.8$ per cent.

The *acetyl* derivative crystallises from methyl alcohol in colourless, prismatic needles which sinter at 114° and melt at $123\text{--}124^\circ$. It is sparingly soluble in cold methyl alcohol.

The *methyl ether*, obtained in the usual way, was identified with 4:5-dinitroveratrole.

2-Hydroxy-3-methoxyphenanthraphenazine was obtained from 4:5-dinitroguaiacol in the manner described above for the preparation of an analogous substance from 5:6-dinitroguaiacol. It crystallised best from carbon disulphide in silky, yellow threads

melting at 239—240°, and dissolving in sulphuric acid to a rich magenta solution.

3:5:6-Trinitroguaiacol (VI).

It was not found practicable further to nitrate 4:6-, 5:6-, or 4:5-dinitroguaiacol, but the 3:5-isomeride was readily converted into a trinitroguaiacol. 3:5-Dinitroguaiacol (40 grams) was dissolved in nitric acid (200 c.c., D 1.42), and any rise of temperature was checked by cooling in running water. After half an hour, a certain amount of the product had crystallised from the solution, and water (300 c.c.) was added and as much salt as would dissolve in the solution. The precipitate was collected, washed with a little brine, and then with the minimum of dilute hydrochloric acid, and dried in the air (38 grams). The substance crystallised from benzene in needles containing solvent of crystallisation, and from chloroform in yellow prisms, which melt at 129° with vigorous decomposition, and evolution of much gas at a slightly higher temperature. This decomposition is not accompanied by charring, and is apparently a smooth process resulting in definite products. When the substance was heated quite gently in a test-tube, there was a mild explosion and the production of relatively much hydrocyanic acid was observed. In combustions, a low result was always obtained for carbon, but the composition of the substance is fixed by other experiments, which are described below. The substance dissolves in water to an intensely yellow solution resembling in appearance a solution of potassium chromate, and on the addition of hydrochloric acid the colour changes to that of a dilute solution of picric acid, and the substance crystallises in prisms. Silk and wool are dyed from aqueous solutions, the former in greenish-yellow and the latter in orange-yellow shades. The trinitroguaiacol also resembles picric acid in forming sparingly soluble salts with bases, and it may be employed as an alkaloidal precipitant.

Attempts were made to compare its molecular weight with that of picric acid by titration of both nitrophenols with a solution of a basic dye, with which each compound forms a sufficiently sparingly soluble salt. After a number of trials, it was found that Rhodamine 6G gave satisfactory results. The method was the following. The nitrophenol solution was mixed with salt and a solution* of Rhodamine 6G containing approximately 1 gram in 500 c.c. of water gradually added with constant stirring to ensure formation of the additive product and in order to avoid premature salting out of the dye. When the supernatant liquid appeared to

* It was unnecessary to ascertain the exact strength of the solution.

have a slight fluorescence, the end-point was near, but not reached until a filtered portion of the solution had a faint pink colour. The reason for this is that when the concentration of nitrophenol is low, the rhodamine salt appears to be just sufficiently soluble to exhibit fluorescence in solution. It was found best to make a rough experiment first, and to repeat it in order to obtain the exact result:

0.2386 Gram of picric acid dissolved in water and made up to 250 c.c.

25 c.c. with 20 grams of salt required 56.2 c.c. of Rhodamine 6G solution.

0.2255 Gram of trinitroguaiacol dissolved in water and made up to 250 c.c.

25 c.c. with 20 grams of salt required 59.9 c.c. of Rhodamine 6G solution.

Whence, assuming equivalence of picric acid and trinitroguaiacol in regard to rhodamine base, M.W. = 258.

$C_7H_5O_6N_3$ requires M.W. = 259.

Pyridine Salt.—This highly characteristic derivative separates in slender, canary-yellow needles when a drop of pyridine is added to a dilute aqueous solution of trinitroguaiacol. It crystallises from methyl alcohol in long, yellow needles melting at $194-195^\circ$ when quickly heated, but if slowly heated, the melting point may be found as low as 180° , or more usually in the neighbourhood of 185° . This behaviour is due to the decomposition which accompanies the melting, and is apparently slow at 180° . As the substance is very readily prepared and purified, it was used to prove that 3:5:6-trinitroguaiacol is the only product of the nitration of 3:5-dinitroguaiacol, and in this case the specimens were always compared by simultaneous heating:

0.2257 gave 0.3549 CO_2 and 0.0561 H_2O . C = 42.9; H = 2.8.

$C_7H_5O_8N_3.C_5H_5N$ requires C = 42.8; H = 3.0 per cent.

This derivative was isolated from the mother liquors from the crystallisation of 3:5:6-trinitroguaiacol, and also from the original nitric acid solution from which the crude product was separated. It was useful as a means of isolating the trinitroguaiacol from aqueous solution, and could be employed directly for the preparation of the trinitroveratrole described below.

3:5:6-Trinitroveratrole (VII).

This ether was readily obtained by the methylation of trinitroguaiacol or its pyridine salt by means of methyl sulphate and

sodium carbonate in boiling xylene solution. Care was taken to ensure reaction between the phenol and sodium carbonate before raising the mixture to the boiling point, since, although the sodium salt is comparatively stable, the free trinitroguaiacol undergoes decomposition in boiling xylene solution. Also, hot aqueous sodium carbonate has some action on the trinitroveratrole, and the xylene solution is accordingly poured away from the excess of sodium carbonate after the reaction, and then submitted to distillation in a current of steam. The pale brown powder which remains in the flask when the solvent has been removed is collected and crystallised from acetic acid, and then from alcohol. The substance is obtained in very pale yellow needles melting at 174° , and sparingly soluble in alcohol, acetic acid, or chloroform, but readily so in ethyl acetate or acetone. The solution in the latter solvent is yellow, and becomes orange on the addition of a drop of ammonia:

0.1317 gave 0.1710 CO_2 and 0.0335 H_2O . $\text{C}=35.4$; $\text{H}=2.8$.

$\text{C}_8\text{H}_7\text{O}_8\text{N}_3$ requires $\text{C}=35.1$; $\text{H}=2.6$ per cent.

The substance is sensitive to alkalis, and is decomposed slowly by cold aqueous sodium hydroxide and by boiling aqueous sodium carbonate. It reacts with primary and secondary bases with elimination of a nitro-group, but the products were not closely examined. On boiling with a concentrated solution of sodium sulphite, the substance is attacked, and in this and other respects it exhibits greater reactivity than the isomeric 3:4:5-trinitroveratrole. On the addition of salt to the resulting yellow solution, a pale yellow substance separated in flat needles, and this material had the properties that would be associated with the expected product, namely, *sodium 3:5-dinitroveratrole-6-sulphonate*.

3:5-Dinitro-2:6-diaminoanisole (VIII).

This substance was readily prepared by boiling 3:5:6-trinitroveratrole with an excess of methyl-alcoholic aqueous ammonia under reflux for half an hour. The red product crystallised from the hot solution, and, after cooling, was collected and several times crystallised from ethyl acetate. It is obtained in garnet needles which soften at 225° and melt at 237° , and is sparingly soluble in most organic solvents. In general character it resembles the isomeride which is obtained from 3:4:5-trinitroveratrole:

0.0981 gave 0.1331 CO_2 and 0.0319 H_2O . $\text{C}=37.0$; $\text{H}=3.6$.

$\text{C}_7\text{H}_9\text{O}_5\text{N}_4$ requires $\text{C}=36.8$; $\text{H}=3.5$ per cent.

The substance is devoid of basic character, and on boiling with dilute aqueous sodium hydroxide, ammonia is evolved and a corre-

sponding nitrophenol obtained. On acidifying the solution, the latter is precipitated in orange-yellow, flat needles.

4:6-Dinitro-1:2:3-trimethoxybenzene (IX).

3:5:6-Trinitroveratrole yielded a bright orange-red solution on the addition of powdered potassium hydroxide to its suspension in methyl alcohol, and, on boiling, the colour gradually faded, and finally a yellow solution was obtained. On the addition of water, an oil separated, and after a short time this crystallised and was collected. The aqueous solution was proved to contain a nitrite. The substance was readily soluble in most organic solvents, but sufficiently sparingly so in methyl alcohol for purposes of crystallisation. It was obtained in pale yellow needles melting at 85°:

0.1262 gave 0.1936 CO_2 and 0.0462 H_2O . $\text{C}=41.8$; $\text{H}=4.1$.

$\text{C}_9\text{H}_6\text{O}_7\text{N}_2$ requires $\text{C}=41.9$; $\text{H}=3.9$ per cent.

The constitution of this compound follows from its conversion by heating during three days in a sealed tube at 100° with methyl-alcoholic ammonia into the dinitrodiaminoanisole described above, and confirmation is found in the observation that on reduction a diamine is produced which does not condense with phenanthraquinone to a derivative of phenazine.

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LVI.—*The Propagation of Flame through Tubes of Small Diameter.*

By WILLIAM PAYMAN and RICHARD VERNON WHEELER.

It has been shown in a previous communication (T., 1917, 111, 1044) that the speed of the "uniform movement" of flame in a given mixture of methane and air is dependent on the diameter of the tube along which the flame travels, being enhanced by the action of convection currents in tubes of large diameter and reduced by conduction of heat by the walls in tubes of small diameter.

If the diameter of the tube is sufficiently small, the "uniform movement" of flame does not develop, but the flame dies out after travelling a few centimetres. Still further reduction in the diameter of the tube renders it impossible for the flame to spread

any measurable distance from the point of ignition. This fact was discovered by Davy, and was the starting point of his researches on the construction of a safe lamp for use in coal mines, his observation being: "I found that in tubes of 1/7-inch in diameter explosive mixtures"—of firedamp and air—"could not be fired when they were opened in the atmosphere" ("Collected Works," Vol. 6, p. 11).

Schloësing and de Mondésir (quoted by St. Claire Deville, "Leçon sur la Dissociation," p. 46) and Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], 4, 319) experimented on this subject, and the last-named have placed on record the speeds of flame in a mixture of methane and air containing 10·4 per cent. of methane, using tubes of glass of different diameters, as follow:

Diameter of tube, mm.	3·2	5·5	8·0	9·5	12·2
Speed of flame, cm. per sec....	nil	22	39	41	47

The methane used by Mallard and Le Chatelier was prepared from sodium acetate, and was impure; nevertheless, their observation that flame would not propagate in glass tubes of 3·2 mm. internal diameter is in fair agreement with Davy's statement (one-seventh of an inch is equal to 3·63 mm.).

Following on his discovery that a tube of small diameter would not allow flame to pass through it, Davy experimented with other means of exposing a cooling surface to the flame, such as perforated plates and systems of concentric tubes, and finally produced his wire gauze safety-lamp. A history of the development of the miners' flame lamp from Davy's original design would be out of place here, but it may be said that the retention of the wire gauze to protect the oil- or spirit-flame from inflammable mixtures of firedamp and air seems to have been regarded as essential by the majority of inventors. A few types of lamps have been constructed in which metal plates perforated with fine holes have been used, but no systematic experiments seem to have been recorded, on the lines of Davy's earlier experiments, to determine under what conditions tubes or perforated plates can be regarded as equivalent in safety to the gauze adopted, mainly for its convenience, by Davy.

In connexion with work on the construction of miners' safety-lamps, we have made a number of experiments on the speed of the uniform movement during the propagation of flame in mixtures of methane (firedamp) and air through tubes of small diameter; * on the passage of flame through similar tubes filled with mixtures

* It should be remembered that the uniform movement of flame is developed only when the inflammable mixture is contained in a tube closed at one end and open at the other, ignition being effected at or near the open end.

of methane and air and open at both ends; and on the passage or projection of flame through short tubes of small diameter.

The first series of experiments—on the uniform movement of flame—serves to demonstrate the increased cooling effect of the walls of the tube as its diameter is decreased, and may be regarded as an extension of the work already referred to (*loc. cit.*, p. 1050). The main results are shown in the table on p. 659; the numbers within brackets record distances, in cm., travelled by the flames before they became extinguished; the other numbers record the speeds of the flames in cm. per second, propagation taking place throughout the lengths of the tubes; the word nil indicates that flame could not be seen to spread an appreciable distance from the secondary discharge spark used to cause ignition. Ignition was, in each instance, at a point 3 cm. from the open end of the tube; the flame was allowed to travel 30 cm. from the point of ignition and its speed over a distance of 1 metre then measured; the tubes were 3 metres in length. Each recorded result is the mean of three or four closely agreeing determinations.

There are several points of interest in this table. The apparent limits of inflammability (horizontal propagation of flame) are narrowed as the diameter of the tube is decreased until with a tube 4.5 mm. in diameter only one of the mixtures tested (containing 9.95 per cent. of methane) would propagate flame.

No attempt was made to determine for each tube the exact limiting percentages of methane required for propagation of flame, but the table should supply fairly close approximations. Thus, the tube 5.6 mm. in diameter would have as its lower limit mixture one containing less than 8.5, but more than 8.25 per cent. of methane, and as its higher limit mixture one containing more than 10.5, but less than 10.65 per cent. Bearing in mind the fact that the exact limiting mixtures were not obtained, it will be seen that the speeds of the flames tend towards a constant value of about 35 cm. per sec. as the limiting mixtures are approached. This speed can be regarded as the slowest at which continued propagation of flame in mixtures of methane and air is possible.

It follows that the higher the coefficient of conductivity of the material of which tubes of small diameter are made, the narrower are the limits of inflammability for a tube of given diameter and the larger is the diameter of tube capable of preventing the spread of flame in any mixture. Thus Davy (*loc. cit.*) found that "metallic tubes prevented explosion better than glass tubes."

In Fig. 1 a curve is given showing the relationship between the speed of the uniform movement in a 9.95 per cent. methane-air mixture and the diameter of the tube (of glass) along which the

Internal diameter of tube. Mm.	Methane in mixture. Per cent.															
	7.6	8.0	8.25	8.4	8.5	9.0	9.5	9.95	10.15	10.5	10.65	10.8	11.0	11.5	11.6	11.65
3.6	nil	nil	nil	nil	nil	nil	nil	nil*	nil	nil	nil	nil	nil	nil	nil	nil
4.5	nil	nil	(20)	(18)	(20)	(20)	(20)	33.5	nil	nil	nil	nil	nil	nil	nil	nil
5.6	(25)	(20)	(27)	—	36.3	38.4	40.8	41.2	40.8	38.4	nil†	nil†	nil	nil	nil	nil
7.2	(37)	(30)	(30)	(30)	38.0	40.5	46.8	46.3	44.5	42.9	(60)	(33)	nil	nil	nil	nil
8.1	(45)	(30)	(35)	36.5	39.3	42.4	47.7	47.4	46.7	44.0	42.2	41.0	(43)	nil†	nil†	nil
9.0	(55)	32.6	34.8	—	40.4	44.4	48.9	48.0	47.9	46.5	45.5	—	42.5	39.0	35.3	(60)

When the flame was started in a tube 5.6 mm. in diameter and 8 cm. long it travelled 30 cm. along the 3.6 mm. tube and then died out.

* Flame travelled towards the open end of the tube, a distance of 3 cm.

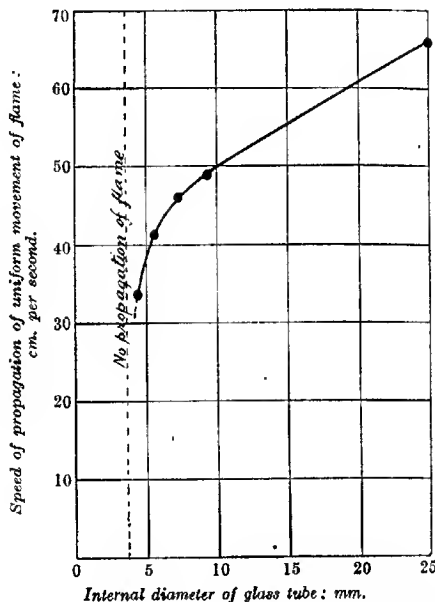
† Flame travelled towards the open end of the tube, a distance of 3 cm.

flame travelled. This curve is a continuation of that shown in Fig. 4 in T., 1917, 111, 1053, and should be compared therewith.

The Passage of Flame through Tubes Open at Both Ends.—

When a mixture of methane and air contained in a horizontal tube open at both ends is ignited near one end of the tube, flame begins to travel with increasing speed towards the other end.* After a certain distance of travel, the flame vibrates backward and for-

FIG 1.



ward, and, in tubes of small diameter, becomes extinguished during any particularly rapid vibration. The distance travelled by the flame before vibrations begin depends on the length and diameter of the tube and on the percentage of methane in the mixture, being greater the longer is the tube and the larger its diameter, and less the nearer the percentage of methane approaches that required to give the fastest speed of flame (9.5 to 10 per cent. of methane in air).

Unless the mixture is a "limit mixture," when the speed of the flame is uniform throughout its progress.

It thus results that a length of tube of diameter small enough to prevent the passage of flame in a mixture containing, say, 10 per cent. of methane in air, may fail to do so when the mixture contains only, say, 7 per cent., despite the fact that the flame in the former mixture has the greater speed. For the reason that with the 10 per cent. mixture vibrations, engendered by the rapidity with which the flame begins to move, may cause self-extinction of the flame, whilst with the 7 per cent. mixture the flame may move comparatively slowly and undisturbed throughout its course.

This fact is illustrated in the series of experiments recorded in the table that follows. The tubes were of glass and were 100 cm. long:

Percentage of methane in mixture	Distances travelled by flame in tubes open at both ends.		
	10.0	8.5	7.5
Internal diameter of tube.			
3.6 mm.	nil.	nil.	nil.
4.4 "	11.5 cm.	10 cm.	75 cm.
6.4 "	14	25 to 30	15 to 20
7.2 "	20 to 25	throughout	throughout.

Experiments of a similar nature were made with tubes of brass. The brass tubes were used as connexions between two open glass tubes 2.5 cm. in diameter and 10 cm. long, as described in the experimental portion of this paper, and their lengths were gradually shortened until flame passed from one glass tube to the other, when a mixture of methane and air was ignited near the open end of one of them. Two series of experiments were made; in one the propagation of flame was horizontal, in the other from below upwards. The results can be tabulated as shown on p. 661.

The lengths of brass tube recorded in this table represent relative distances of travel of the flames, the actual distances travelled being from 1 to 1.5 cm. less in each instance. The results for horizontal propagation of flame are shown graphically in Fig. 2, from which the greater precautions necessary to prevent the passage of flame in mixtures containing the lower percentages of methane is apparent.

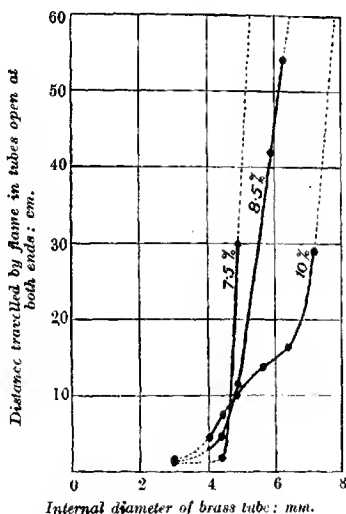
The conditions under which an inflammation of firedamp takes place within a miners' safety-lamp depend on the construction of the lamp and on the manner in which it is manipulated. With some types of lamps (those receiving their air-supply from below the wick), the conditions are similar to those obtaining in the experiments just described. With others—and these constitute the majority of types—the air-supply reaches the wick from above, so that when firedamp is present in the air an inflammable mixture may occupy most of the upper portion of the lamp before it becomes

Percentage of methane in mixture.	Internal diameter of tube. Mm.	Lengths of brass tube required to prevent the passage of flame. Cm.					
		10.0		8.5		7.5	
		Horizontal propagation.	Upward propagation.	Horizontal propagation.	Upward propagation.	Horizontal propagation.	Upward propagation.
		less than 2	less than 2	less than 2	less than 2	less than 2	less than 2
	4	4 to 5	5 to 6	2 to 3	5	less than 2	less than 2
	4.4	7.5	9	4 to 5	7.5	less than 2	less than 2
	4.8	10	11.5 to 12.5	11.5	18 to 19	less than 2	less than 2
	5.6	14	15 to 16	42 to 43	50	30	30
	6.4	16	18	54	55	—	—
	7.2	29	32	more than 60	more than 60	—	—

ignited. Ignition is then as if near the closed end of a tube open at the other end.

Experiments were made in which a glass tube 12 cm. long and 2 cm. in diameter, closed at one end, was used as an explosion-vessel. Brass tubing of different diameters could be attached to the open end and determinations made of the lengths required to prevent the transmission of flame to an inflammable mixture of methane and air when a similar mixture was ignited by a secondary discharge 15 mm. from the closed end of the explosion-vessel, the apparatus being fixed horizontally.

FIG. 2.



With mixtures of methane and air containing either 10 or 7.5 per cent. of methane, the passage of flame from the explosion-vessel to the atmosphere outside was prevented by less than 2 cm. length of brass tubing of any diameter up to the largest tried, namely, 8 mm. In many instances, tongues of slightly luminous gases were projected from the ends of the brass tubes, but inflammation of the surrounding mixture did not follow. The question therefore arose whether increasing the speed of projection of these hot gases, by increasing the length of the explosion-vessel, would enable them to retain sufficient heat to ignite a mixture of methane

and air even after their passage through a considerable length of brass tubing of small diameter.

Experiments were therefore made in which explosion-vessels, 2 cm. in diameter, of different lengths were employed, so that the flames in 10 per cent. mixtures of methane and air, ignited at the closed ends of the explosion-vessels, would acquire different speeds by the time they reached the open ends. Previous experiments had shown that the speed of flame in a 10 per cent. mixture of methane and air contained in a horizontal glass tube 2 cm. in diameter, closed at one end and open at the other, increases progressively with its distance of travel from the closed end over distances of 3 or 4 metres. The results were as follow:

Length of explosion-vessel. Cm.	Length of brass tube required to prevent passage of flame in a 10 per cent. methane-air mixture. Cm.			
	12	20	30	40
Internal diameter of brass tube. Mm.				
4	less than 2	less than 2	less than 2	3 to 4
4.4	"	3 to 4	"	3 to 4
4.8	"	13 to 14	16 to 18	more than 30
5.6	"	16 to 18	24 to 25	"
6.4	"	18 to 19	more than 30	"
7.2	"	19 to 20	"	"
8.0	"	19 to 20	"	"

The increased speed imparted to the heated products of combustion by increasing the speed of the flame thus materially reduces the protection against inflammation of the external atmosphere afforded by brass tubes. A miners' safety-lamp, however, rarely has an effective length of "explosion-vessel" exceeding 12 to 15 cm. On the other hand, its diameter is often as great as 6 cm. It seemed possible that the use of an explosion-vessel of larger diameter than that employed in the series of experiments just described might have an effect similar to increasing its length, inasmuch as the higher pressures produced within a vessel of greater capacity would project the heated products of combustion through the brass tubes with greater speed.

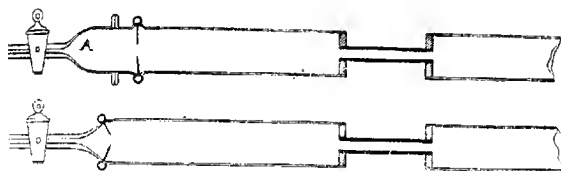
On trial, however, this was found not to be so. An explosion-vessel 7.5 cm. in diameter and 12 cm. long was no more effective in transmitting inflammation through brass tubes to the external atmosphere than one 2 cm. in diameter. Furthermore, when the length of this larger explosion-vessel was increased to 40 cm., it was found that protection was still afforded by a length of brass tube of less than 2 cm. of any diameter up to 8 mm., the largest tried. Increasing the capacity of the explosion-vessel thus actually

decreased the danger of the inflammation being conveyed to the external atmosphere.

These results, which were repeated many times with mixtures of different methane-content, are in conformity with some remarkable experiments by Beyling ("Verein für die Bergbaulichen Interessen im oberbergamtbezirk Dortmund." Essen, 1906), made primarily to determine the best means of rendering electrical machinery flame-proof. Beyling used an explosion-vessel 33.5 cm. in diameter and 42.5 cm. long (capacity, 42 litres), and found that when a mixture of firedamp and air containing 9 per cent. of methane was ignited at one end of the vessel, a hole more than 4 cm. in diameter could exist at the other end without danger of a similar mixture outside being ignited.

The explanation of these results is that the products of combustion, being under a fairly high pressure within the explosion-vessels of large capacity, were rapidly expanded as they issued

FIG. 3.



through the holes or tubes, and were thus cooled below the temperature at which they could ignite the mixture outside.

EXPERIMENTAL.

The experimental work can be divided into two portions, that dealing with the speed of flame in tubes of small diameter, and that relating to the passage of flame through short lengths of such tubes from vessels filled with inflammable mixtures.

The motion of the most rapid flame studied was sufficiently slow to follow by eye, so that for the measurements of speeds it sufficed to record the times at which the flames made their appearance at fixed points along the tubes. This was done by the use of a tapping-key in electrical connexion with a chronograph.

The different forms of apparatus used in the experiments on the passage of flame through short lengths of tubes are shown in Fig. 3. The upper diagram illustrates the means employed to study the passage of flame through tubes open at both ends. The ground-

glass cover, *A*, was removed just before igniting the mixture by sliding it downwards, so as to avoid disturbance of the mixture within the tube. The whole apparatus, including the glass extension beyond the length of brass tube undergoing test, was filled with the requisite mixture by displacement of air, six times the volume of the apparatus being taken for displacement.

The lower diagram shows the arrangement when testing the conditions necessary for the passage of flame from a closed vessel, and is self-explanatory.

The methane used throughout the experiments was from fire-damp obtained from a blow in South Wales; it contained 2 per cent. of nitrogen as its only impurity. The mixtures were stored over water in metal or glass gas-holders of suitable capacity, and were analysed before use.

These experiments have been carried out for the Mines Department of the Home Office. They complete part of a research on miners' safety-lamps which will form the subject of an official report.

[Received, July 12th, 1918.]

LVII.—*The Relative Activities of Methyl, Ethyl, and n-Propyl Iodides with Sodium α - and β -Naphthoxides.*

By HENRY EDWARD COX.

THE reactivity of the alkyl iodides with a variety of compounds has been measured by many investigators.

It has usually been found that methyl iodide is many times more active than ethyl iodide, and ethyl iodide is from one to five times as active as *n*-propyl iodide; several anomalies have been recorded, however, including one instance in which ethyl iodide is twice as reactive as methyl iodide. It seemed of interest to examine the relative activities of these substances with further bases, and as the naphthoxides are very similar in chemical behaviour, it was decided to examine whether there is any difference in their reactivities with the alkyl haloids; methyl, ethyl, and *n*-propyl iodides were chosen, as it has been found in all recorded work that the higher members of the series show a perfectly regular and gradual diminution in activity with increasing molecular

N-PROPYL IODIDES WITH SODIUM α - AND β -NAPHTHOXIDES. 667

weight, whereas the first three members have shown considerable divergence.

The following table shows the results on record for these iodides calculated in terms of *n*-propyl iodide=1:

	Methyl	Ethyl	<i>n</i> -Propyl
Triethylamine in acetone ¹	590.7	5.24	1.00
Sodium ethoxide in ethyl alcohol ²	36.13	2.85	1.00
Potassium ethoxide „ „ „ ²	35.53	2.78	1.00
Sodium methoxide „ „ „ ²	16.31	2.51	1.00
Potassium methoxide „ „ „ ²	16.41	2.45	1.00
Dimethylaniline „ „ „ ²	48.00	3.2	1.00
Triethylaniline „ „ „ ²	327.0	4.2	1.00
Sodium ethyl acetoacetate „ „ „ ⁴	39.2	4.2	1.00
Silver nitrate „ „ „ ⁵	0.94	2.2	1.00
Sodium phenoxide „ „ „ ⁶	12.1	2.5	1.00

¹ Menshutkin, *Zeitsch. physikal. Chem.*, 1890, 5, 589.

² Hecht, Conrad, and Bruckner, *ibid.*, 1889, 4, 273, 649.

³ Preston and Jones, T., 1912, 101, 1930.

⁴ Wislicenus, *Annalen*, 1882, 212, 239.

⁵ Burke and Donnan, T., 1904, 85, 555.

⁶ Segaller, T., 1913, 103, 1154.

There are also many figures on record for methyl and ethyl iodides only. In the above table, there is a very marked increase in activity of methyl iodide with triethylamine and with triethylaniline, which contrasts very strongly with the fact that ethyl iodide is twice as reactive as methyl iodide with silver nitrate.

It is well known that the naphthols are esterified more readily than the phenols, so that it might be anticipated that the velocity constants would be higher than with phenoxides and lower than with ethoxides. This expectation is borne out by the results obtained.

Sodium α -naphthoxide is slightly more reactive than the β -compound, and it was found that the difference is slightly accentuated as the molecular weight of the alkyl group increases; thus at concentration *N*/5, the ratio k_α/k_β is:

Methyl iodide.....	1.12
Ethyl iodide	1.23
<i>n</i> -Propyl iodide	1.32

This greater activity of the α -compound with *n*-propyl iodide makes the relative activity of the iodides rather less with the α - than with the β -naphthoxide. At the same concentration, *N*/5, was found:

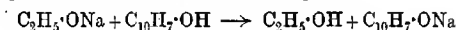
	α -Naphthoxide.	β -Naphthoxide.
Methyl iodide	7.41	8.82
Ethyl iodide	1.99	2.16
<i>n</i> -Propyl iodide	1.00	1.00

These results all refer to the reaction in ethyl alcohol at 40°. The reaction is bimolecular, as is to be expected from the equation.

There is, however, a possibility of a side-reaction taking place, such as the formation of olefines or ethers. This is suggested by the fact that the velocity constant decreases slightly as the reaction proceeds; this decrease has been observed by nearly all workers with alkyl iodides. It does not seem probable that it is due to loss of alkyl iodide, as it is observed even at low temperatures and when working in sealed tubes. It is also observed in the presence of an excess of alkyl iodide. The decrease is not due to neutral-salt action, as it is found that addition of sodium iodide has no appreciable effect on the velocity constant.

It was also observed that, particularly in the more concentrated solutions, the reaction mixture, which is practically colourless at the start, darkens as the reaction proceeds. This takes place even though the flask is not opened or exposed to the air. The colour is not due to the liberation of iodine.

The question also arises whether the equation,



is reversible or not. If alcoholysis takes place, sodium ethoxide will be formed; the velocity coefficients for sodium ethoxide and the alkyl iodides are several times larger than those of the naphthoxides with the corresponding iodides. The velocity constant would therefore show a markedly higher value at the commencement of an experiment, and would rapidly fall off as the ethoxide disappears, and the increasing concentration of free naphthol retards the further alcoholysis of the naphthoxide. A rapid decrease in the value of the constant would be found if there is much alcoholysis.

In the experiments here described, there is a gradual diminution in the value of the constant, but it is not large; indeed, in most experiments it is not larger than the decrease observed by Hecht and Conrad in their work on the ethoxides, where the case of alcoholysis does not arise. In order to obtain some information on this point, experiments were made in *N*/10-solution with methyl iodide and sodium α - and β -naphthoxides containing 5 per cent. excess of the corresponding naphthol; this would suppress alcoholysis, and consequently decrease the constant. The effect observed was that the constant is decreased by 7.3 per cent. in the case of the α -naphthoxide and by 10.7 per cent. in the case of the β -naphthoxide, but there was still observed the gradual decrease in the value of *k*.

The effect of the increased viscosity by the excess of naphthol

would no doubt slightly decrease the constant, but not to so great an extent. It is interesting to note that Robertson and Acree (*Amer. Chem. J.*, 1913, **49**, 474) found that a decrease of 7 per cent. was produced by 5 per cent. excess of phenol in the reaction between sodium phenoxide and methyl iodide at concentration $N/2$.

Effect of Initial Concentration on the Velocity Coefficients.

This point is one of considerable importance. Hecht, Conrad, and Brückner (*Zeitsch. physikal. Chem.*, 1890, **5**, 289) proposed the formula $k_v = k_1 + a \log v$, where v is the volume in litres which would contain one gram-molecular weight of the reacting substances.

This empirical equation has been found to hold remarkably well in several reactions of the kind here considered. Schröder and Acree (*T.*, 1914, **105**, 2582) have given a scientific basis to this equation, which greatly enhances its interest. They show also that at a given dilution corresponding with complete ionisation of one of the reacting substances, the equation would no longer hold.

The effect of initial concentration has been tried by measuring the velocity of the reaction in equivalent concentrations from $N/1$ to $N/40$. The velocity coefficient increases with dilution in each case, and it increases more rapidly in the case of the α -naphthoxide than with the β -naphthoxide.

The increase is large with methyl iodide, less with ethyl and still less with n -propyl iodide; this is quite in accord with the results of Hecht, Conrad, and Brückner. The equation $k_v = k_1 + a \log v$ is found to hold for ethyl and propyl iodides at least up to dilution $v=40$. With methyl iodide and the α - and β -naphthoxides, the equation holds from $v=1$ up to $v=10^*$ and $v=7$ respectively; thereafter the value of k_v increases abnormally rapidly. Figs. 1 and 2, obtained by plotting actual values of k against $\log v$, show the increase with dilution. Each point lying off the straight line has been determined in duplicate.

It is most unlikely that ionisation of the naphthoxides would be complete at as low a dilution as $N/10$, so that Schröder and Acree's prediction cannot be applied.

Also, if the increase is due to alcoholysis or ionisation, or to any change in the naphthoxide, it would be expected that a similar rise would be observed with ethyl and propyl iodides at perhaps slightly greater dilution.

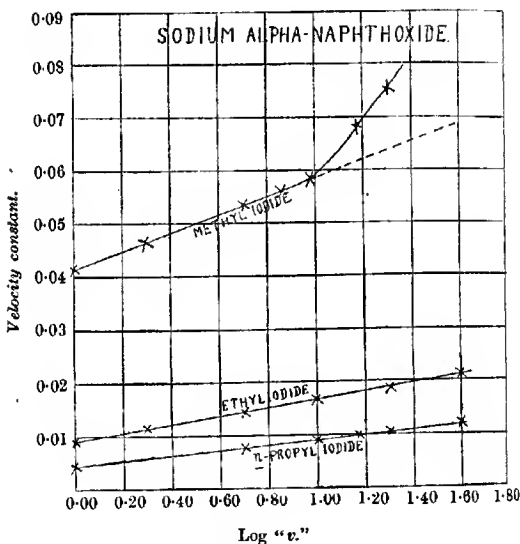
Up to $v=40$, no such rise is observed, so that it appears probable that this abnormality is due to some specific effect with methyl iodide only.

EXPERIMENTAL.

All the reactions were carried out with ethyl alcohol as solvent; the alcohol was prepared by digesting commercial absolute alcohol with calcium oxide and calcium for several hours, and then re-distilling from calcium.

The naphthoxides were prepared from the purest obtainable α - and β -naphthols, quite white, melting at 94° and 122° respectively. The calculated quantity of sodium dissolved in ethyl alcohol was added to an alcoholic solution of the naphthol, and the

FIG 1.



solution evaporated to dryness in a vacuum at 100° . The products were almost white. (Found: Na=13.75 and 13.87 respectively. Calc.: Na=13.86 per cent.)

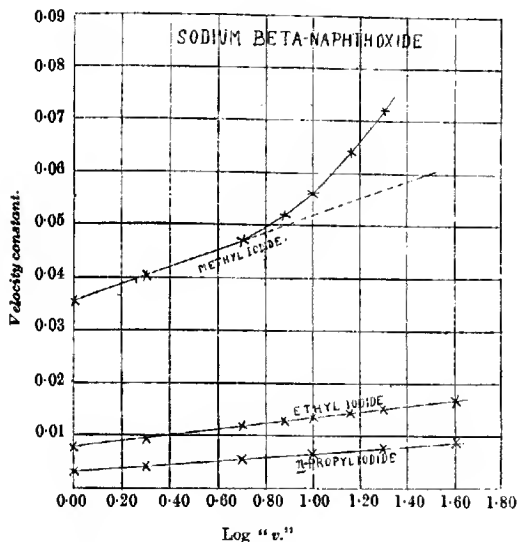
Some of the duplicate experiments were made by mixing solutions of sodium ethoxide and naphthol in the proper proportions just before use. This method gave results identical with those obtained by weighing out the dry compound, and has been applied

successfully by Hecht and Conrad and by Robertson and Acree in their work on phenoxides. It is very convenient in the case of the α -naphthoxide, as this salt is very sensitive to air and moisture and rapidly turns brown on exposure.

Tymstra and Eggink's method (*Ber.*, 1906, **39**, 14) was tried, but without success, minute balls of sodium being retained even after prolonged heating.

Methyl and ethyl iodides were purified by washing with dilute alkali, then with water, drying over fused calcium chloride, and

FIG. 2.



redistilling from ignited silver. The boiling points were 42.5–43° and 71.5–72° respectively. *n*-Propyl iodide was obtained from propyl alcohol by Bancel's method (*Bull. Soc. chim.*, 1883, [ii], **39**, 648) and purified as above. It boiled at 101–101.5°.

The temperature was maintained at 40.0° by means of a thermostat fitted with an Ostwald toluene regulator and an efficient stirring gear.

The requisite quantities of reagents were weighed out, dissolved separately, and the solutions mixed. After allowing time for the

mixture to attain the temperature of the bath, 5 c.c. were withdrawn by a pipette, kept at 40°, calibrated to deliver a volume equal to 5 c.c. at 15°.

This was run into cold water containing almost enough standard hydrochloric acid to neutralise the unchanged naphthoxide, and the titration completed as rapidly as possible, using lacmoid as indicator.

The results were calculated from the equation $k' = \frac{1}{t \cdot a \cdot (a-x)}$ in terms of c.c. of acid used for titration, then brought to k in terms of gram-molecules per litre by multiplying by five times the dilution " v " of the acid. Time in minutes was reckoned from the time of the first titration when the mixture had attained the proper temperature.

Only one experiment with each pair of substances is given in full, the other results being summarised for economy of space.

Methyl Iodide.

Sodium α -naphthoxide.			Sodium β -naphthoxide.		
$N/1$ each.	Acid $N/5$.		$N/1$ each.	Acid $N/5$.	
t .	$a-x$.	k' .	t .	$a-x$.	k' .
0	23.35	—	0	21.70	—
7	18.25	0.001719	14	15.05	0.001451
15	14.70	0.001680	21	13.05	0.001455
22	12.65	0.001646	30	11.15	0.001454
30	1.00	0.001603	41	9.65	0.001404
37	9.75	0.001614	50	8.65	0.001390
44	8.85	0.001595	60	7.75	0.001382
Mean $k' = 0.001643$.			Mean $k' = 0.001423$.		
$k = k' \times 25 = 0.04108$.			$k = k' \times 25 = 0.03558$.		

Ethyl Iodide.

Sodium α -naphthoxide.			Sodium β -naphthoxide.		
$N/5$ each.	Acid $N/10$.		$N/5$ each.	Acid $N/10$.	
t .	$a-x$.	$k' \times 10^4$.	t .	$a-x$.	$k' \times 10^4$.
0	9.85	—	0	9.70	—
60	8.43	0.2850	85	8.08	0.2376
130	7.18	0.2905	160	7.10	0.2359
234	5.95	0.2845	235	6.33	0.2335
290	5.43	0.2850	300	5.78	0.2330
350	5.00	0.2813	360	5.43	0.2261
410	4.65	0.2769	420	5.05	0.2260
Mean $k' = 0.0002839$.			Mean $k' = 0.0002318$.		
$k = k' \times 50 = 0.01420$.			$k = k' \times 50 = 0.01159$.		

n-Propyl Iodide.

Sodium α -naphthoxide.			Sodium β -naphthoxide.		
N/10 each.	Acid = N/20.		N/10 each.	Acid = N/20.	
t.	$\alpha-x$.	$k' \times 10^4$.	t.	$\alpha-x$.	$k' \times 10^4$.
0	9.55	—	0	9.65	—
140	8.55	0.8748	140	8.85	0.6693
247	7.90	0.8856	247	8.35	0.6532
384	7.30	0.8406	384	7.80	0.6402
540	6.65	0.8456	540	7.25	0.6363
586	6.48	0.8464	587	7.02	0.6616
630	6.35	0.8376	630	6.90	0.6555
Mean $k' = 0.0008551$.			Mean $k' = 0.0006525$.		
$k = k' \times 100 = 0.08551$.			$k = k' \times 100 = 0.06525$.		

Summary of Results.

Methyl Iodide.

Sodium α -naphthoxide.			Sodium β -naphthoxide.		
v.	k_r (found).	k_r (calc.).	k_r (found).	k_r (calc.).	
1	0.04108	0.04108	0.03556	0.03556	
2	0.04693	0.04623	0.04060	0.04059	
5	0.05307	0.05303	0.04725	0.04723	
7.5	0.05555	0.05604	0.05235	0.05019	
10	0.05864	0.05813	0.05590	—	
15	0.06844	—	0.06487	—	
20	0.07513	—	0.07209	—	
"a" = 0.0171.			"a" = 0.0167.		

Ethyl Iodide.

Sodium α -naphthoxide.			Sodium β -naphthoxide.		
v.	k_r (found).	k_r (calc.).	k_r (found).	k_r (calc.).	
1	0.009185	0.009185	0.007900	0.007900	
2	0.01166	0.01135	0.009908	0.009646	
5	0.01422	0.01422	0.01159	0.01195	
7	—	—	0.01250	0.01280	
10	0.01636	0.01638	0.01402	0.01370	
15	—	—	0.01453	0.01472	
20	0.01860	0.01855	0.01568	0.01545	
40	0.02109	0.02072	0.01700	0.01719	
"a" = 0.00720.			"a" = 0.00580.		

n-Propyl Iodide.

Sodium α -naphthoxide.			Sodium β -naphthoxide.		
v.	k_r (found).	k_r (calc.).	k_r (found).	k_r (calc.).	
1	0.004300	0.004300	0.003160	0.003160	
5	0.007133	0.007355	0.005355	0.005431	
10	0.008551	0.008670	0.006525	0.006410	
20	0.01011	0.009985	0.007392	0.007388	
40	0.01121	0.001130	0.008517	0.008367	
"a" = 0.00437.			"a" = 0.00325.		

674 THE RELATIVE ACTIVITIES OF METHYL, ETHYL, ETC.

Sodium α -naphthoxide containing 5.0 per cent. excess of α -naphthol with methyl iodide, $N/10$ each.

$k=0.05436$; decrease in $k=7.30$ per cent.

Sodium β -naphthoxide containing 5.0 per cent. excess of β -naphthol with methyl iodide, $N/10$ each.

$k=0.04989$; decrease in $k=10.75$ per cent.

Conclusions.

The reaction of the alkyl iodides with sodium α -naphthoxide and sodium β -naphthoxide is a bimolecular one of a special type, in which the velocity of reaction is dependent on the initial concentration.

There is some evidence that both naphthoxides undergo alcoholysis in ethyl-alcoholic solution.

Sodium α -naphthoxide is more reactive towards the alkyl iodides than is sodium β -naphthoxide.

The presence of an excess of α - or β -naphthol decreases the velocity coefficient.

The velocity of the reaction in each case increases with dilution. The increase is most marked with methyl iodide, and becomes less as the molecular weight of the alkyl group increases.

The velocity of reaction at dilution " v " can be expressed in the form of an equation $k_v = k_1 + a \log v$. This equation holds good with ethyl and n -propyl iodides at least so far as dilution $v=40$. With methyl iodide, the equation holds only up to dilution $v=10$ for sodium α -naphthoxide and $v=7$ for the β -compound; at higher dilution, methyl iodide exhibits abnormal reactivity.

The order of relative activity is methyl, ethyl, n -propyl. Methyl iodide is several times more active than ethyl iodide at the same dilution; this is in agreement with the majority of the published results for these iodides.

The author wishes to express his thanks to Mr. G. R. Thompson, who has provided every facility for this work; also to Dr. J. C. Crocker for his kind interest and valuable advice.

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LVIII.—*The Ternary System—Sodium Sulphate, Ammonium Sulphate, and Water. The Utilisation of Nitre Cake for the Production of Ammonium Sulphate.*

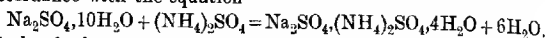
By HARRY MEDFORTH DAWSON.

IN connexion with experiments instituted with the object of finding a method for the separation of sodium sulphate and ammonium sulphate from solutions containing both these substances, and with a view to the possible use of solutions of nitre cake for the absorption of ammonia in the manufacture of ammonium sulphate, an investigation has been made of the equilibrium relations in the system $\text{Na}_2\text{SO}_4\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$. This investigation was completed during 1917, and although it was originally intended to defer the publication of the results for the present, the appearance of a series of papers by Matignon and Meyer (*Compt. rend.*, 1917, **165**, 787; 1918, **166**, 115, 686) on the equilibrium conditions in this system has led the author to revise his original proposal.

The components of this system combine to form two compounds, namely, Glauber's salt and the double salt $\text{Na}_2\text{SO}_4\cdot(\text{NH}_4)_2\text{SO}_4\cdot 4\text{H}_2\text{O}$, and the characteristic features of the system are largely determined by the properties of these compounds. The double salt seems to have been first obtained by Séguin (*Ann. Chim. Phys.*, 1814, **91**, 219), and subsequently its formation by the interaction of ammonium chloride and Glauber's salt and by the action of water on a mixture of sodium chloride and ammonium sulphate was described by Schiff (*Annalen*, 1860, **114**, 68). The crystallographic properties of the double sulphate have been examined on several occasions by Mitscherlich (*Ann. Phys. Chem.*, 1843, [ii], **58**, 469), Lang (*Wien Akad. Ber.*, 1862, **45**, 108), Reinsch (*Zeitsch. Kryst. Min.*, 1884, **9**, 561), and Retgers (*Zeitsch. physikal. Chem.*, 1891, **8**, 58), but the conditions of formation of the double salt and its relation to the simple salts do not appear to have been previously examined. According to Retgers (*loc. cit.*), crystals of the anhydrous double sulphate separate out at temperatures between 50° and 70°, but the crystals actually obtained by this observer were very small and impure, and the view that they represent the anhydrous double sulphate was based on the optical behaviour of the crystals when examined under the microscope.

In preliminary experiments, it was found that finely powdered Glauber's salt and ammonium sulphate react together at the

ordinary temperature, the mixture becoming pasty and the temperature falling considerably. Although it was at first suspected that this might be due to the simple dehydration of the Glauber's salt in the presence of ammonium sulphate, further experiments showed that the reaction consists in the formation of the double salt in accordance with the equation



If the finely powdered substances are mixed together whilst the temperature is kept at -15° to -20° , there is no evidence of the above reaction, the mixture remaining perfectly dry, but at -10° , on the other hand, the mixture shows distinct signs of caking, and it thus seemed probable that the above reaction sets in at some temperature between -10° and -20° .

Lowering of the Temperature of Transition of Glauber's Salt on the Addition of Ammonium Sulphate.—In experiments made to determine the effect of ammonium sulphate on the temperature at which Glauber's salt is transformed into anhydrous sodium sulphate, about 100 grams of Glauber's salt were heated to about 40° and cooling curves taken before and after the addition of measured quantities of ammonium sulphate. During the cooling, the tube containing the mixture was surrounded by cotton-wool and the mixture thoroughly stirred. The results obtained are shown in table I.

TABLE I.

Reference number.	Nature of cooling system.	Transition temperature.
<i>a</i>	Glauber's salt.	32.35°
<i>b</i> 100 grams	Glauber's salt + 4.66 grams $(\text{NH}_4)_2\text{SO}_4$	30.05°
<i>c</i>	" " + 9.33 " "	27.75°
<i>d</i>	" " + 18.65 " "	26.50°
<i>e</i>	" " + 26.60 " "	26.50°
<i>f</i>	" " + 43.8 " "	continuous fall in temperature.

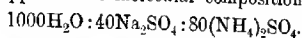
The value of the molecular lowering of the transition temperature calculated from observations *b* and *c* is 65, which is slightly less than the value obtained by Loewenherz (*Zeitsch. physikal. Chem.*, 1895, **18**, 70) for relatively dilute solutions of the alkali sulphates. The limiting temperature, 26.5° , obviously represents an invariant point, and, in point of fact, the three solid phases in equilibrium with the solution are Glauber's salt, anhydrous sodium sulphate, and the double salt $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$.

Decomposition of the Double Salt.—In view of Retgers's observation that the crystals deposited at higher temperatures are anhydrous, it was to be expected that the double salt would decom-

pose at some temperature below 70° . Preliminary experiments, in which a dilatometer was filled with the finely powdered double salt, gave no positive evidence of this change. On the other hand, when a mixture of 50 grams of Glauber's salt and 30 grams of ammonium sulphate was heated to about 80° and allowed to cool in the air, the temperature remained stationary at $58-59^{\circ}$. In a further experiment, in which the tube containing the mixture was jacketed and allowed to cool with the outside tube immersed in a water-bath at 50° , the temperature of the mixture fell slowly to 58.2° and then rose to 59.3° , at which it remained constant for a very considerable time. This temperature was evidently to be regarded as that corresponding with a further invariant point, and it seemed probable that this was the temperature of decomposition of the hydrated double salt.

Solubility Measurements.—Further information was sought by solubility measurements, the chief object of which was to ascertain the composition of the solutions which are characteristic of the invariant and univariant systems. In the case of the invariant systems, the solutions in question are saturated with respect to three solid phases, and the temperature has a definite value. On the other hand, the temperature is variable in the case of the univariant systems which are characterised by the presence of two solid phases, but at a given temperature the concentration of both the sodium sulphate and the ammonium sulphate has a definite value.

In connexion with the solubility measurements, a quantity of the double salt was prepared by dissolving sodium sulphate and ammonium sulphate in the molecular proportion 1:2 to give a solution of the approximate molecular composition



The warm solution was allowed to cool to the ordinary temperature, and crystals of the double salt were deposited, which, after drying in contact with the air, gave on analysis $\text{Na}_2\text{SO}_4 = 40.7$ (theory, 41.0 per cent.) and $(\text{NH}_4)_2\text{SO}_4 = 38.3$ (theory, 38.15 per cent.).

Preliminary measurements of the quantities of sodium and ammonium sulphates in the solutions saturated at 0° , 25° , 50° , and 100° were made in order to ensure the presence of the requisite solid phases in the subsequent experiments. In making the final determinations, a solution having approximately the composition of the saturated solution was prepared, and when the temperature of this had been brought to the desired value, the requisite solid phases in finely powdered form were added in considerable quantity. The mixture was stirred for one to two hours, and a sample of the saturated solution, filtered through a cotton-wool plug, was removed.

for analysis. The sodium sulphate was estimated by evaporation of a measured fraction to dryness in a platinum dish, and subsequently heating the residue to redness. It was found advisable to treat the residue with a little ammonia, and to repeat these operations before the sodium sulphate was finally weighed. For the estimation of the ammonium sulphate, a second fraction was added to an excess of standard sodium hydroxide, and, after boiling, the excess of alkali was titrated by means of standard acid.

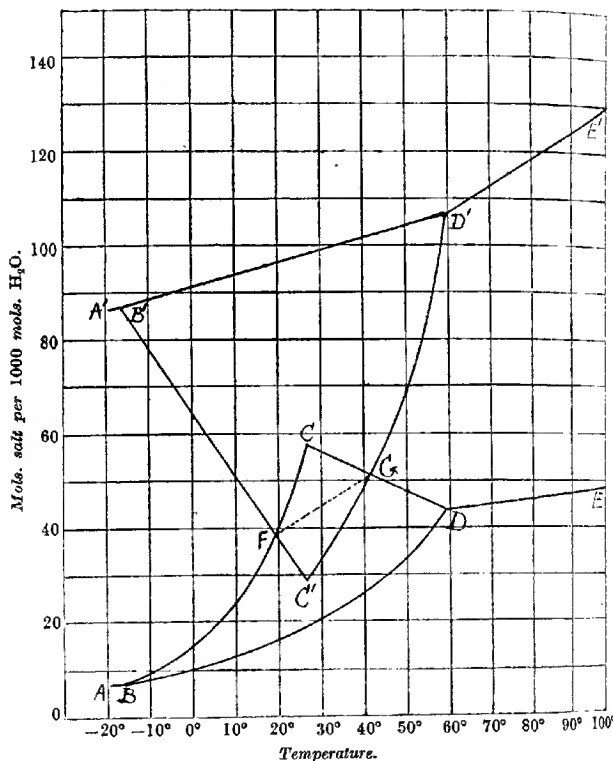
The results obtained in the solubility experiments are shown in table II, in which are recorded the temperature, the nature of the solid phases in contact with the solution, and also the weight and molecular composition of the solution.

The relations exhibited by the solubility data recorded in the table on p. 679 are shown in Fig. 1, in which temperature is given by the abscissa, whilst the ordinate represents the number of molecules of sodium sulphate or ammonium sulphate per 1000 molecules of water. Two groups of curves are thus obtained, the lower one of which has reference to the sodium sulphate content of the saturated solutions and the higher one to the amount of ammonium sulphate. Corresponding points in the two groups are indicated by the same letters, the ammonium sulphate group being distinguished by a dash. The points *D* and *D'* thus represent the numbers of molecules of sodium sulphate and ammonium sulphate respectively per 1000 molecules of water in the solution which is characteristic of the invariant system at the temperature of decomposition of the double salt into the component simple sulphates. In exactly the same way, the curves which connect such corresponding points are corresponding curves. The curves which represent solutions saturated with respect to Glauber's salt and ammonium sulphate (*AB* and *A'B'*), with respect to double salt and ammonium sulphate (*BD* and *B'D'*), and with respect to anhydrous sodium sulphate and ammonium sulphate (*DE* and *D'E'*), do not exhibit any peculiarity which calls for special comment. The case is different, however, when we consider the curves which correspond with solutions saturated with respect to double salt and Glauber's salt, and those which represent solutions saturated with respect to double salt and anhydrous sodium sulphate. The curves *BC* and *B'C'* show that in solutions saturated in regard to double salt and Glauber's salt, the sodium sulphate content increases rapidly with rise of temperature, whilst the ammonium sulphate concentration rapidly decreases. Between -16° , which, according to the curves in Fig. 1, appears to be the temperature of formation of the double salt, and 26.5° , at which Glauber's salt is transformed into the anhydrous sulphate, the

molecular ratio of ammonium sulphate to sodium sulphate in the saturated solution falls from about 12.8 to 0.50.

The curves CD and $C'D'$, which represent solutions saturated with respect to double salt and anhydrous sodium sulphate, follow an opposite course, in that the sodium sulphate content decreases

FIG. 1.
 $\text{Na}_2\text{SO}_4-(\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}$.



with rise of temperature, whilst the ammonium sulphate concentration increases rapidly. Between 26.5° and 59.3° , at which the double salt is decomposed, the molecular ratio of ammonium sulphate to sodium sulphate increases from 0.50 to 2.44.

The point F , at which the curves BC and $B'C'$ intersect, and

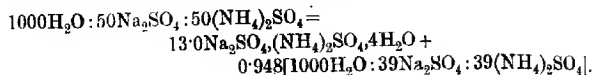
the point G , corresponding with the intersection of CD and $C'D'$, represent respectively the lower and upper limits of the temperature interval within which the double salt is not decomposed in contact with water. The limiting temperatures are approximately 20° and 41.5° respectively, and it is only within this range that solutions saturated with respect to double salt and sodium sulphate (Glauber's salt below 26.5° and anhydrous sodium sulphate above 26.5°) contain a larger molecular quantity of sodium sulphate than of ammonium sulphate. Below 20° , the double salt is decomposed by water with the separation of Glauber's salt, and above 41.5° it is similarly decomposed with the separation of anhydrous sodium sulphate. The dotted curve joining the points F and G represents the curve of solubility of the double salt. In practice, it is possible to measure the solubility of the double salt at temperatures outside the interval corresponding with FG , but the saturated solutions so obtained are meta-stable.

The graph of the solubility data in Fig. 1 shows clearly that the two ammonium sulphate curves, as well as the two sodium sulphate curves, intersect at about -16° , and it is probable that this represents the temperature at which the double salt is formed from Glauber's salt and ammonium sulphate. Further evidence in support of the existence of this lower limiting temperature is afforded by observations on the cooling of certain mixtures of the components. Suitable mixtures are obtained by mixing finely powdered Glauber's salt and ammonium sulphate in the molecular proportion 2:3, with the addition of a little water to reduce the stiffness of the pasty mass which is formed by their interaction. The tube containing this mixture was fitted with a thermometer and stirrer, and surrounded by a wider glass tube immersed in a freezing mixture at -22° . The following readings were taken after successive five-minute intervals: -11.0° , -13.1° , -14.5° , -15.5° , -16.5° , -17.0° , -17.5° , -18.0° , -18.2° , -18.5° , -18.3° , -18.0° , -17.9° , -17.2° , -16.9° , -16.6° , -16.3° , -16.0° , -16.1° , -16.3° , -16.5° . According to this record, the temperature fell to -18.5° and then rose to -16.0° , which represents the temperature of formation of the double salt, and agrees closely with the temperature indicated by the solubility curves.

Crystallisation of Solutions containing Sodium and Ammonium Sulphates.—According to the graph of the solubility data in Fig. 1, it is evident that the crystallisation of a solution, which contains equimolecular quantities of the two sulphates, will yield the pure double salt if the temperature of the solution lies between 20° and 41.5° .

In an actual experiment, in which a solution, prepared by dis-

solving 284 grams of sodium sulphate and 264 grams of ammonium sulphate in 720 grams of water, was allowed to cool to 20°, 180 grams of the double salt were obtained. This result corresponds closely with that calculated from the equation:

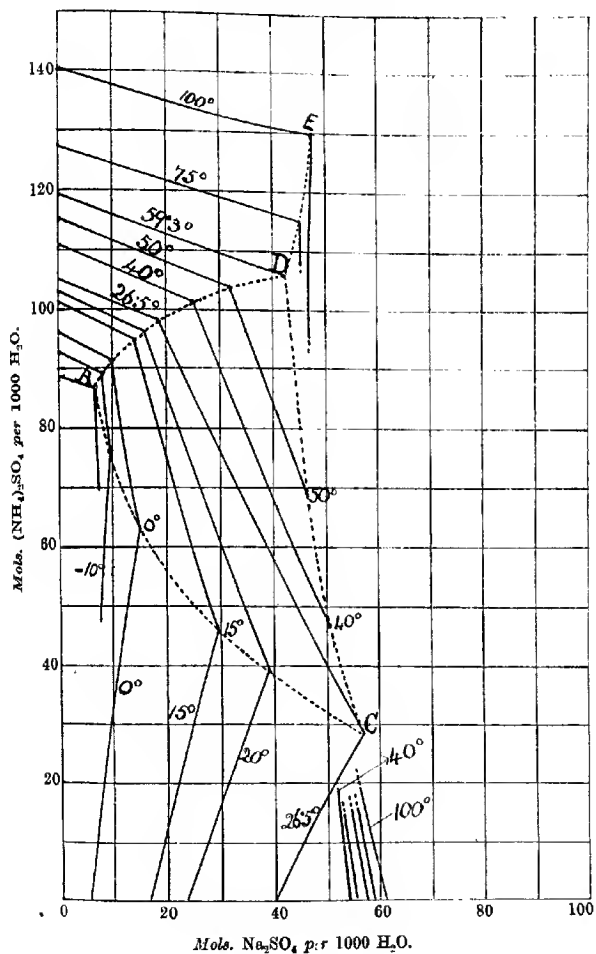
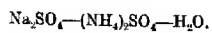


With regard to the separation of sodium and ammonium sulphates by crystallisation from a solution containing the mixed sulphates, it should be noted that there is a great disparity at low temperatures in the quantities of the two sulphates which are contained in solutions saturated with respect to Glauber's salt and ammonium sulphate or the double salt. For such solutions, the value of the molecular ratio of ammonium sulphate to sodium sulphate increases rapidly with rise of temperature until the ratio becomes equal to unity at the upper limit of the lower transition interval (20°). In view of the high value of the ratio at low temperatures, it is obviously possible to crystallise out a large proportion of the sodium sulphate from a solution containing sodium and ammonium sulphates by lowering the temperature.

Although Fig. 1 is well adapted to show the relationship between the double salt and the simple salts, the changes which occur on crystallisation may be more suitably discussed in reference to the curves which are shown in Fig. 2. In this diagram, the composition of any solution is represented by a single point. The horizontal axis gives the number of molecules of sodium sulphate per 1000 molecules of water, and the vertical axis the number of molecules of ammonium sulphate per 1000 of water. In the construction of this diagram, the required data for the solubility of sodium sulphate and of ammonium sulphate in water have been taken from the tables given in Landolt-Börnstein-Meyerhoffer. The isothermal curves connecting the points on the sodium sulphate and ammonium sulphate axes pass through the points which correspond with the saturated solutions recorded in table II. Below -16° and above 59.3°, the isothermals consist of two branches, and between these temperatures there are three branches on each isothermal. The isothermals actually represented on the diagram are those for -10°, 0°, 15°, 20°, 26.5°, 40°, 50°, 59.3°, 75°, and 100°. The sodium sulphate curves corresponding with the five highest temperatures are only indicated in so far as they do not interfere with the clearness of the diagram. The points *B*, *C*, and *D* correspond with the three invariant systems at -16°, 26.5°, and 59.3°, and are indicated by the same letters in Fig. 1.

The dotted curve BD represents the solutions which are saturated with respect to ammonium sulphate and double salt, BC those

FIG. 2.



which are saturated with respect to Glauber's salt and double salt, and *CD* those saturated with respect to anhydrous sodium sulphate and double salt. The region enclosed by the three curves corresponds with solutions which are saturated only with respect to the double salt.

By reference to Fig. 2, it is possible to predict what will occur when any solution containing sodium and ammonium sulphates is crystallised either by the removal of water at constant temperature or by a lowering of the temperature of the solution.

The diagram shows that the isothermal for 26.5° represents the maximum extension of the double salt curve, the molecular ratio of ammonium sulphate to sodium sulphate in the saturated solution varying from 5.2 when saturation with respect to ammonium sulphate is reached to 0.50 when the solution becomes saturated with respect to sodium sulphate. From this it is apparent that, at this temperature, the double salt may be crystallised out from solutions of widely varying composition. On proceeding from 26.5° to higher or lower temperatures, the double salt isothermals undergo a gradual contraction until they disappear at -16° and 59.3° respectively.

From the position of the dotted boundary curves on the diagram, it is evident that the solutions from which the double salt crystallises out between these limiting temperatures contain, in general, an excess of ammonium sulphate. At low temperatures, the required excess of ammonium sulphate is considerable, and for the most part solutions of the two sulphates when crystallised at low temperatures yield Glauber's salt as the solid product. If the concentration of the solution of the mixed sulphates is appropriately adjusted, a large proportion of the sodium sulphate may be removed in the form of Glauber's salt by cooling. Since the separation of Glauber's salt from the solution involves the removal of ten molecules of water for each molecule of sodium sulphate, it follows that the crystallisation will be accompanied by an automatic increase in the concentration of the ammonium sulphate.

The solubility data which determine the extent to which the separation of sodium and ammonium sulphates may be effected by crystallisation of Glauber's salt are recorded in table III for temperatures of -10.0° and -15.0° . The successive columns give the temperature, the nature of the solid phases, the molecular composition of the solution in terms of 1000 molecules of water, and the molecular ratio of ammonium sulphate to sodium sulphate in the saturated solution. The data cover the entire range of the Glauber's salt curves at the two temperatures, and by plotting the results it is possible to obtain the ratio of ammonium sulphate to

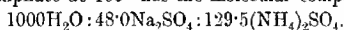
sodium sulphate in any solution which is saturated with respect to Glauber's salt at these temperatures.

TABLE III.

Tem- perature.	Nature of solid phases.	Molecules salt per 1000 mols. H ₂ O.		Mol. ratio (NH ₄) ₂ SO ₄ Na ₂ SO ₄ .
		Na ₂ SO ₄ .	(NH ₄) ₂ SO ₄ .	
-10.0°	Ice and Glauber's salt	7.32	47.2	6.45
-10.0	Glauber's salt	7.95	52.0	6.54
-10.0	"	8.51	60.4	7.10
-10.0	Glauber's salt and double salt	9.86	76.5	7.76
-15.0	Ice and Glauber's salt	7.48	69.7	9.3
-15.0	Glauber's salt	7.53	76.0	10.1
-15.0	Glauber's salt and double salt	7.20	84.0	11.7

The numbers in the last column show that the molecular ratio of ammonium sulphate to sodium sulphate in the solutions saturated with respect to Glauber's salt increases with increase in the ammonium sulphate content. Taking the value of the molecular ratio which corresponds with the middle portion of the isothermal, it follows that crystallisation at -10.0° will yield a mother liquor containing about seven molecules of ammonium sulphate per molecule of sodium sulphate, and at -15° a mother liquor containing ten to eleven molecules of ammonium sulphate per molecule of sodium sulphate.

If such mother liquors are evaporated at or about 100° , a large proportion of the ammonium sulphate present may be obtained in a pure condition. By reference to table II, it will be found that the solution saturated with respect to sodium sulphate and ammonium sulphate at 100° has the molecular composition



For this solution, the molecular ratio of ammonium to sodium sulphate is equal to 2.7. If, therefore, we have a mother liquor for which, as a result of the separation of Glauber's salt by cooling to -15° , the molecular ratio of ammonium to sodium sulphate has been increased to 10.5 (compare table III), it follows that

$\frac{10.5 - 2.7}{10.5} \times 100 = \text{approximately } 75 \text{ per cent. of the contained ammonium sulphate may be obtained in pure condition by evaporation at } 100^{\circ}.$

The relations exhibited by the equilibrium conditions at low temperatures and in the neighbourhood of 100° have been made the basis of a method for the production of ammonium sulphate and Glauber's salt by the treatment of solutions of the mixed sulphates such as are obtained when nitro cake or mixtures of

nitre cake and sulphuric acid are employed for the absorption of ammonia (Brit. Patent 114236, 1918). In this process, the liquor from the ammonia saturator has its concentration suitably adjusted, and is then cooled to about -10° , at which temperature a considerable proportion of the sodium sulphate separates out in the form of Glauber's salt. The mother liquor is then transferred to an evaporator, and on evaporation of the solution, crystals of ammonium sulphate are deposited until the molecular ratio of ammonium sulphate to sodium sulphate in the hot liquid has been reduced to a value not less than about 2.7. The residual liquor is then suitably diluted and returned to the refrigerator in admixture with a further quantity of solution from the saturator.

In view of the fact that the liquid from the saturator inevitably contains a certain amount of free acid, it was of some interest to investigate the influence of the presence of free sulphuric acid on the crystallisation of Glauber's salt at low temperatures. In these experiments, solutions containing fixed quantities of sodium sulphate and ammonium sulphate and variable quantities of free sulphuric acid were cooled to -10.0° , and the composition of the mother liquors was determined. The results obtained are recorded in table IV, in which the composition by weight and the molecular composition of the resulting solutions are shown, in addition to the value of the molecular ratio of ammonium sulphate to sodium sulphate.

TABLE IV.

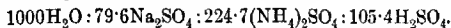
	Grams per 100 of water.			Molecules per 1000 of water.			Mol. ratio (NH_4) ₂ SO ₄ Na ₂ SO ₄
	Na ₂ SO ₄ .	(NH ₄) ₂ SO ₄ .	H ₂ SO ₄ .	Na ₂ SO ₄ .	(NH ₄) ₂ SO ₄ .	H ₂ SO ₄ .	
a	6.19	38.05	—	7.85	51.9	—	6.61
b	6.48	37.9	3.98	8.21	51.7	7.31	6.30
c	6.61	37.7	7.95	8.38	51.4	14.6	6.13

Although the ratio of ammonium sulphate to water in the three mother liquors is not quite the same, the values are sufficiently close to permit of a comparison of the effect of the free acid on the separation of the Glauber's salt, and it is evident from the table that the molecular ratio of ammonium sulphate to sodium sulphate in the solution decreases as the proportion of free acid increases. In other words, the separation of Glauber's salt is less complete in the presence of free acid, but the influence of the acid is not such as to affect seriously the efficiency of the cooling process. It may be noted that the mother liquor in experiment *c* contains about 5.2 per cent. of free sulphuric acid.

With regard to the influence of free acid on the separation of

ammonium sulphate by evaporation of the mother liquor obtained in the previous cooling process, it has been found that the molecular ratio of ammonium sulphate to sodium sulphate, which is characteristic of the acid-free solution when saturated with respect to sodium and ammonium sulphates at 100° , is not appreciably altered in the presence of a considerable quantity of free acid.

An experiment in which this ratio was determined in the presence of free sulphuric acid may be quoted. Fifty grams of a sulphuric acid solution of the approximate molecular composition, $1000\text{H}_2\text{O}:100\text{H}_2\text{SO}_4$, were placed in a tube provided with a stirrer and heated at 100° . Excess of finely powdered sodium and ammonium sulphates was added, and the mixture stirred for about an hour, when a sample of the solution was found to have the molecular composition,



The molecular ratio of ammonium to sodium sulphate in the saturated solution, which, it may be noted, contains about 15 per cent. of free acid, is thus 2·8, whilst the value of this ratio for the acid-free solution is 2·7.

The results of the observations in acid solutions lead to the conclusion that the presence of free acid in moderate quantities does not affect to more than a small extent either the separation of Glauber's salt by crystallisation at low temperatures or the separation of ammonium sulphate by evaporation of the resulting mother liquor.

Summary.

The equilibrium relations in the ternary system $\text{Na}_2\text{SO}_4-(\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}$ between -20° and 100° are described and illustrated by diagrams.

The characteristic features of the system are in a large measure determined by the double salt $\text{Na}_2\text{SO}_4\cdot(\text{NH}_4)_2\text{SO}_4\cdot4\text{H}_2\text{O}$, which is formed from Glauber's salt and ammonium sulphate at -16° , and decomposes with the formation of the anhydrous simple salts at $59\cdot3^{\circ}$.

Between -16° and 20° , the double salt is decomposed by water with the formation of Glauber's salt, and between $41\cdot5^{\circ}$ and $59\cdot3^{\circ}$ it is decomposed with the formation of anhydrous sodium sulphate.

The temperature at which Glauber's salt is transformed into the anhydrous sulphate is depressed to $26\cdot5^{\circ}$ by the addition of ammonium sulphate. At this temperature, the solution formed is in equilibrium with Glauber's salt, anhydrous sodium sulphate, and the double salt.

It is shown that sodium sulphate and ammonium sulphate may

be separated from one another by subjecting solutions of appropriate concentration to low temperatures, when most of the sodium sulphate crystallises out in the form of Glauber's salt. A large proportion of the ammonium sulphate in the mother liquor may be obtained in pure condition by evaporation at 100°.

The method of separation is not appreciably affected by the presence of moderate quantities of free sulphuric acid.

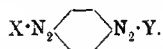
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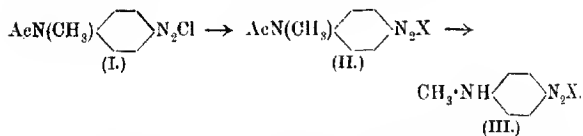
LIX.—*Acylated p-Phenylenemethyldiamines.*

By GILBERT T. MORGAN and WILLIAM ROBINSON GRIST.

THE acyl derivatives of *p*-phenylenediamine have long had considerable technical importance, owing to the circumstance that these derivatives afford a practicable method of diazotising this diamine in both its amino-groups, a process required in the manufacture of hisazo-colouring matters containing the complex:



It has also been found that the monodiazonium salts (I) of the acyl derivatives of *p*-phenylenemethyldiamine are utilisable in the production of aminoazo-dyes (III), the acyl group being removed by hydrolysis from the intermediate product, which has the general formula II:



In certain cases, the acylaminoazo-compounds themselves are found to have useful tinctorial properties (Morgan and Micklethwait, *J. Soc. Dyers*, 1909, 25, 107; *Farbenfabriken vorm. F. Bayer & Co.*, D.R.P. 296964).

The *p*-aminomethylacylanilides can be prepared by the following methods:

(i) From methylaniline, by successively acylating this base, nitrating its acyl derivative, and reducing the *p*-nitro compound.

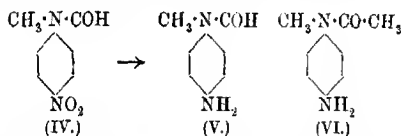
(ii) By methylating the acylanilide and then subjecting the methylacylanilide to the same treatment as in method (i).

(iii) Successive methylation and acylation of *p*-nitroaniline, followed by reduction of the resulting *p*-nitromethylacylanilide.

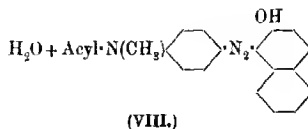
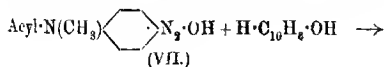
(iv) Methylation of the alkali derivative of 4:4'-dinitrodiazaminobenzene, and hydrolysis of the methylated diazoamine to a mixture of chlorobenzene and methyl-*p*-nitroaniline, the secondary nitro-base being then acylated and reduced (Morgan and Alcock, T., 1909, 95, 1332).

Of these four methods, the first is generally the most practicable providing that methylaniline is available in sufficient amount. Being in possession of considerable quantities of this base obtained by the process indicated in English Patent 514 of 1916, the authors have utilised this means of preparing several intermediate compounds from methylaniline which have not hitherto been described (Eng. Pat. 16520 of 1916).

p-Nitromethylformanilide (IV) is obtainable by nitrating methylformanilide, this acyl derivative being readily prepared by warming methylaniline with concentrated formic acid. It was shown that in the main product of this nitration the nitro-group enters the para-position with respect to the acylamino-complex, this orientation being demonstrated by hydrolysing the nitro-compound to *p*-nitromethylaniline and by converting this secondary base into its characteristic nitrosoamine.



p-Aminomethylformanilide (as-formyl-*p*-phenylenemethyldiamine) (V) results from the reduction of the new nitro-derivative. Methylacetanilide, readily obtainable by mixing together methylaniline and acetic anhydride, is successively converted into *p*-nitromethylacetanilide and *p*-aminomethylacetanilide (as-acetyl-*p*-phenylenemethyldiamine) (VI). These two *p*-aminomethylacyl-



anilides when treated with nitrous anhydride in dry acetone solution give rise to diazohydroxides (VII), which combine readily with dry β -naphthol, the condensation being accompanied by the elimination of a molecular proportion of water.

The *acylmethylaminobenzenediazo- β -naphthols* (VIII) thus produced are identical with the products obtained by successively diazotising the *p*-aminomethylacylanilides in aqueous solution and combining the diazonium salt with alkaline β -naphthol.

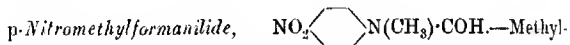
The foregoing diazohydroxides are obtainable as colourless, amorphous solids soluble in acetone and insoluble in ether or water.

p-Aminomethylbenzanilide and *p*-aminoethylbenzanilide when subjected to the action of nitrous anhydride in acetone solution yield only oily diazo-derivatives (compare Morgan and Alcock, *loc. cit.*).

EXPERIMENTAL.

I. *p*-Aminomethylformanilide and its Acetyl Homologue.

The starting point in these preparations was methylaniline, prepared by treating aniline with formaldehyde in the presence of zinc dust and sodium hydroxide (Eng. Pat. 514 of 1916). Methylformanilide was produced by heating the secondary base with one part of concentrated commercial formic acid for eight hours, and obtained as a viscid oil, which was extracted with benzene.



formanilide (three parts) was dissolved in eight parts of cold concentrated sulphuric acid and nitrated with a mixture of two parts of nitric acid (D 1.42) and an equal volume of concentrated sulphuric acid. The nitration was carried out at 0° to 10° , and the product poured on ice. The pale yellow precipitate was crystallised from alcohol, when it separated in pale yellow, prismatic crystals melting at $118\text{--}120^\circ$:

0.1643 gave 23.2 c.c. N_2 at 20° and 752 mm. $\text{N}=16.03$.

$\text{C}_8\text{H}_8\text{O}_3\text{N}_2$ requires $\text{N}=15.55$ per cent.

When hydrolysed with hot concentrated hydrochloric acid, *p*-nitromethylformanilide yielded successively *p*-nitromethylaniline (m. p. 152°) and *p*-nitrophenylmethylnitrosoamine (m. p. 100°), thus demonstrating the orientation of the entrant nitro-group. The yield of *p*-nitromethylformanilide from a series of batches was about 70 per cent. The acid mother liquors slowly deposited a more readily soluble nitro-compound, which, being contaminated with resinous by-products, was not further investigated.

p-Aminomethylformanilide (as-Formyl-*p*-phenylenemethyldiamine).—*p*-Nitromethylformanilide (10 grams) was added gradually to a mixture of 10 grams of iron filings, 0.5 gram of formic acid, and 30 c.c. of water at 50°. The mixture was agitated vigorously, and the temperature, which tended to rise rapidly after each addition, was not allowed to exceed 75°. After the addition of all the nitro-compound, the heating was continued at this temperature for a few minutes, and the mixture was then treated with an excess of calcium carbonate and filtered quickly while hot. The *p*-aminomethylformanilide separated in feathery needles on cooling, and a further crop was obtained from the washings of the residue concentrated in a stream of carbon dioxide. The crude product was crystallised from water, separating therefrom in grey needles melting at 129–130°:

0.2213 gave 35.4 c.c. N₂ at 19° and 761 mm.* N=18.68.

C₈H₁₀ON₂ requires N=18.66 per cent.

p-Aminomethylformanilide was obtained by crystallisation from light petroleum in colourless needles melting at 132°. It darkened on exposure to light and air, especially when in a moist condition.

p-Aminomethylacetanilide.—Methylacetanilide was prepared by adding acetic anhydride (30 grams) to an equal weight of methylaniline. Much heat was generated, and, after cooling, the solution was poured into an equal volume of water. The acetyl compound remained oily for several days, but was caused to solidify by mixing with 2 c.c. of concentrated ammonia solution.

Methylacetanilide (m. p. 100°), recrystallised from alcohol, was dissolved in four parts of concentrated sulphuric acid and nitrated at 0° to 12° with 1.3 parts of nitric acid (D 1.42) mixed with an equal volume of concentrated sulphuric acid. The product obtained by pouring the solution on ice and crystallisation from alcohol melted at 153°. It was reduced by the method already described in the case of the formyl derivative (above).

p-Aminomethylacetanilide separated in brown needles, and was purified by crystallisation from hot water, when it was obtained in greyish-white needles melting at 60°:

0.1320 gave 18.4 c.c. N₂ at 19° and 768 mm. N=16.39.

C₉H₁₂ON₂ requires N=17.07 per cent.

Further crystallisation from light petroleum gave colourless needles of the base melting at 63°. On exposure to air, the base assumed a yellow colour.

* In this and subsequent analyses the nitrogen was measured over potassium hydroxide (50 grams in 100 grams of water).

II. Diazo-derivatives of *p*-Aminomethylacylanilides.

Formylmethylaminobenzene-4-diazo-hydroxide.—A solution of *p*-aminomethylformanilide in dry acetone (twenty-five parts) was cooled to -10° and treated with excess of nitrous anhydride dissolved in the same solvent. The diazo-compound, which was obtained as a greyish-white, granular precipitate by the addition of cooled dry ether, darkened rapidly on exposure:

0.2060 gave 41.8 c.c. N_2 at 22.5° and 767 mm. $N=23.55$.

$C_8H_8O_2N_2$ requires $N=23.46$ per cent.

This product after drying over quicklime in a partial vacuum decomposed violently at $131-132^{\circ}$. When mixed with dry β -naphthol, the desiccated diazo-hydroxide combined to form an azo-derivative with loss of water, the mixture becoming damp.

Acetylmethylaminobenzene-4-diazo-hydroxide.—The foregoing treatment with nitrous anhydride applied to *p*-aminomethylacetanilide led to the production of a colourless, granular deposit of diazo-hydroxide precipitated by ether from the acetone solution. The product on exposure to air and light assumed a pale yellow colour:

0.2018 gave 38.8 c.c. N_2 at 22° and 766 mm. $N=22.30$.

$C_9H_{11}O_2N_2$ requires $N=21.76$ per cent.

The dried diazo-hydroxide decomposed violently at $131-132^{\circ}$, and when triturated with β -naphthol it combined to form an azo-derivative, water being eliminated.

Comparative experiments on the diazotisation of *p*-aminomethylbenzanilide and *p*-aminoethylbenzanilide with nitrous anhydride in acetone led only to oily diazo-derivatives which formed azo-compounds with β -naphthol and similar phenolic substances (compare Morgan and Alcock, T., 1909, 95, 1323).

III. Azo-derivatives of *p*-Aminomethylformanilide and *p*-Aminomethylacetanilide.

Formylmethylaminobenzene-4-azo- β -naphthol,



—This compound was prepared by direct combination between formylmethylaminobenzene-4-diazo-hydroxide and dry β -naphthol or from the diazonium chloride of *p*-aminomethylformanilide prepared in aqueous solution and combined with alkaline β -naphthol. The azo- β -naphthol separated as a dark purple solid, insoluble in

aqueous alkalis, but dissolving in alcohol to a magenta solution. It separated from this solution in ill-defined crystals, which, after washing with ether, melted at 160—161°.

0.1426 gave 17.3 c.c. N_2 at 25° and 763 mm. $N=13.81$.

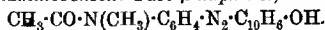
$C_{18}H_{15}O_2N_3$ requires $N=13.76$ per cent.

p-Aminomethylformanilide was diazotised and combined with the following phenolic substances: salicylic acid, α -naphthol-4-sulphonic acid (N and W acid), and 8-amino- α -naphthol-3:6-disulphonic acid (H acid), giving rise to a series of azo-dyes, the properties of which are tabulated below.

Azo-derivatives of p-Aminomethylacylanilides.

Base.	Phenolic compound.	Colour.	Azo-dye.		Colour with concentrated sulphuric acid.
			Dyeing effect on wool (a) and silk (b).		
<i>p</i> -Amino-methyl-form-anilide.	Salicytic acid	orange-brown powder.	a. brownish-yellow	b. lemon-yellow	orange-brown
	β -Naphthol	ill-defined dark red nodules			crimson
	"N & W" acid	dark red powder	russet brown	brownish-red	reddish-brown
	"H" acid	deep purple powder	brownish-purple	"royal" purple	dark brownish-red, crimson on dilution.
<i>p</i> -Amino-methyl-acet-anilide.	Salicytic acid	brownish-yellow powder	greenish-yellow	golden-yellow	bright orange-brown
	β -Naphthol	well-defined red needles			bright crimson
	"N & W" acid	orange-red powder	scarlet	scarlet	reddish-brown
	"H" acid	purple powder	bluish-purple reddened by meta-chrome mordant	"Bordeaux" red	crimson

Acetyl/methylaminobenzene-4-azo-β-naphthol,



—This azo-derivative was obtained by grinding together acetyl-methylaminobenzene-4-diazo-hydroxide and β-naphthol; the mixture rapidly turned red and became moist owing to the elimination of water due to the azo-condensation. It was also prepared by diazotising *p*-aminomethylacetanilide in cold concentrated hydrochloric acid, the solution of the soluble diazonium chloride being added to alkaline β-naphthol. The product crystallised from alcohol in well-defined, transparent, red tablets or flattened needles melting at 139°:

0.1414 gave 16.1 c.c. N₂ at 17° and 766 mm. N = 13.34.

C₂₀H₁₇O₂N₃ requires N = 13.15 per cent.

p-Aminomethylacetanilide was also combined with several other phenolic substances, giving rise to the above azo-dyes.

The authors desire to express their thanks to Mr. A. W. H. Upton, A.C.G.F.C., for assistance in the preliminary experiments of this investigation.

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Organic Chemistry.

Oxidation Products of Paraffin Wax. AKTIEN-GESELLSCHAFT FÜR MINERALÖL-INDUSTRIE VORM. FANTO & Co. (*Zeitsch. angew. Chem.*, 1918, **31**, i, 115).—The method of oxidising paraffin wax by means of atmospheric oxygen was not discovered by Bergmann as he suggests (this vol., i, 285), but by Freund in 1915.

C. A. M.

Besson's Method for the Preparation of Chloroform from Ethyl Alcohol. K. UKITA (*J. Chem. Ind., Tokyo*, 1918, **21**, 219—216).—A stream of chlorine gas is passed into 100 grams of alcohol until the product has D 1.299, when it is added to a mixture of 500 grams of bleaching powder, 100 grams of milk of lime, and 2 litres of water, and the liquid is distilled. The yield is 95—98 grams of chloroform. During the treatment of the alcohol with chlorine, the liquid separates into two layers; the heavy layer increases gradually, and when the chlorination is satisfactory the liquid again becomes homogeneous. J. F. B.

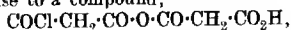
Some Fluoro-bromo-compounds of the Methane and Ethane Series. HANS RATHSBURG (*Ber.*, 1918, **51**, 669—672).—Completely brominated compounds react with silver fluoride to form fluoro-bromo-derivatives. Thus, carbon tetrabromide and silver fluoride in the molecular proportion 1:2 react at above 50—60° to form *fluorotribromomethane*, CBr_3F , as a colourless, heavy, pleasant-smelling liquid, b. p. 107°/760 mm., which is insoluble in water. This reacts with more silver fluoride, best at 140—150°, giving *difluorodibromomethane*, a mobile, readily soluble liquid, b. p. 24.5°/760 mm., m. p. below -80°. Ethyl tribromoacetate and silver fluoride (1:4) react at 190—200° to give *ethyl fluorodibromoacetate*, an insoluble liquid, b. p. 171—173°/760 mm., which is very readily hydrolysed. J. C. W.

Inhibitory Effects of Water on the Interaction of Aluminium and (a) the Fatty Acids; (b) Phenol, Cresol, and α - and β -Naphthols; (c) Methyl, Ethyl, Butyl, Amyl, and Benzyl Alcohols. RICHARD SELIGMAN and PERCY WILLIAMS (*J. Soc. Chem. Ind.*, 1918, **37**, 159—164. Compare A., 1916, ii, 187).—A continuation of work previously recorded. It is definitely shown that when dry fatty acids, dry alcohols, and substances of a phenolic character are heated with aluminium at the boiling point of the substance in question, there is a rapid action between the metal and the organic compound. If, however, a small amount of water is added to the organic compound, the reaction is prevented, or, if it has already commenced, it is at once inhibited. The reaction

has been studied in the case of (i) a mixture of stearic, palmitic, and oleic acids, (ii) phenol, (iii) cresol (commercial), (iv) α -naphthol, (v) β -naphthol, (vi) methyl alcohol, (vii) ethyl alcohol, (viii) butyl alcohol, (ix) amyl alcohol, and (x) benzyl alcohol. The inhibitory action is explained in the following way. The metal is normally protected by the film which covers it, but this film breaks down when exposed to the attack of the dehydrated substances considered. The presence of even the minutest traces of water is sufficient to inhibit the attack, owing either to the fact that the salts, phenoxides, or alkyl oxides, as the case may be, are immediately decomposed by water, aluminium hydroxide being formed, or because the aluminium exposed by the breakdown of the film is immediately reoxidised by water (compare also Gladstone and Tribe, T., 1881, 39, 9; 1882, 41, 155). J. F. S.

The Decomposition of Glycerol in the Presence of Different Catalysts: Formation of Ethyl and Allyl Alcohols. PAUL SABATIER and GEORGES GAUDION (*Compt. rend.*, 1918, 166, 1033—1039).—The three catalysts used were alumina as a dehydrating catalyst, finely divided copper as a dehydrogenating catalyst, and uranous oxide as a mixed catalyst, capable of producing the two effects. When the vapours of glycerol are passed over alumina at 360°, the products are carbon monoxide, methane, and a trace of carbon dioxide, together with acetaldehyde, which undergoes crotonisation, giving higher aldehydes. Passed over finely divided copper at 330°, the glycerol vapour is decomposed, giving as gaseous products hydrogen and carbon dioxide mixed with some methane and carbon monoxide. The liquid products are ethyl alcohol, allyl alcohol, and some of the higher alcohols. With uranous oxide, more ethyl alcohol and less allyl alcohol are obtained, and more acetaldehyde. Further, the proportion of carbon dioxide in the gaseous products is increased. By hydrogenation with nickel at 300°, the products are water and the following gases: hydrogen, methane, ethane, and carbon monoxide and dioxide. W. G.

The Action of Fumaryl Chloride on Fumaric Acid. G. C. A. VAN DORP and P. J. MONTAGNE (*Rec. trav. chim.*, 1918, 37, 294—301. Compare *ibid.*, 1906, 25, 96).—When fumaryl chloride and fumaric acid are heated together at 165° and the products of the reaction separated by means of benzene and treated with aniline, there are obtained maleinanilic acid, fumarodanilide, fumaranilic acid, and fumaric acid. The authors suggest that the condensation of fumaryl chloride and fumaric acid first gives rise to a compound,



which with another molecule of fumaryl chloride gives the compound $\text{COCl}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COCl}$, and this may be decomposed by aniline to give fumarodanilide and fumaranilic acid, whilst the intermediate compound gives either fumarodanilide and fumaric acid or fumaranilic acid. W. G.

Methyltetronic Acid and its Amide. C. S. HUDSON and L. H. CHERNOFF (*J. Amer. Chem. Soc.*, 1918, **40**, 1005—1007).—Methyltetronolactone was readily prepared by bubbling air through an aqueous solution of rhamnose containing potassium hydroxide. So prepared, it has m. p. 123°, $[\alpha]_D -44.7^\circ$. When dry ammonia was passed through an ethereal solution of the lactone, *methyltetronamide*, m. p. 135° (decomp.), $[\alpha]_D +54.8^\circ$, was obtained.

[EDGAR T. WHERRY.]—Methyltetronolactone has $n_D 1.500$; $n_D 1.515$; $n_D 1.535$; double refraction strong, 0.085 . The axial angle is large, $2E=120^\circ \pm 10^\circ$. Sign, positive. Methyltetronamide has $n_D 1.510$; $n_D 1.530$; $n_D 1.560$; double refraction very strong, 0.050 . W. G.

The Isomeric Tetra-acetates of *l*-Arabinose and β -Triacetylmethyl *l*-Arabinoside. C. S. HUDSON and J. K. DALE (*J. Amer. Chem. Soc.*, 1918, **40**, 992—997. Compare Chavanne, A., 1902, i, 346).—By the acetylation of *l*-arabinose with acetic anhydride and sodium acetate, α -*l*-arabinose tetra-acetate, m. p. 97° (corr.), $[\alpha]_D^{25} +42.5^\circ$, was obtained. This tetra-acetate when heated on a water-bath with acetic anhydride and zinc chloride gave the isomeric β -*l*-arabinose tetra-acetate, m. p. 86°, $[\alpha]_D^{25} +147.2^\circ$ (corr.). Attempts to prepare α -triacetylmethyl *l*-arabinoside in a crystalline form from either bromoacetyl *l*-arabinose or α -methyl *l*-arabinoside were not successful, but β -triacetylmethyl *l*-arabinoside, m. p. 85° (corr.), $[\alpha]_D^{25} +182.0^\circ$, was readily obtained by acetylating β -methyl *l*-arabinoside. W. G.

Triacetyl-*d*-xylose and d -Triacetylmethyl *d*-Xyloside. C. S. HUDSON and J. K. DALE (*J. Amer. Chem. Soc.*, 1918, **40**, 997—1001).—Bromoacetylxylose when shaken with silver carbonate in acetone solution yielded triacetyl-*d*-xylose, m. p. 138—141° (corr.), having initial rotation $[\alpha]_D^{25} +70.28^\circ$, which dropped after ten days to 40.8° . This compound, when boiled with acetic anhydride and sodium acetate, yielded β -tetracetyl-*d*-xylose. α -Methyl *d*-xyloside on acetylation yielded α -triacetylmethyl *d*-xyloside, m. p. 86° (corr.), $[\alpha]_D^{25} +119.55^\circ$. β -Triacetylmethyl *d*-xyloside was similarly prepared. W. G.

The Glucosazone Reaction. IRA D. GARAND and H. C. SHERMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 955—969).—A study of the conditions governing the yield of glucosazone in the osazone test. The authors find that the correct m. p. of phenylglucosazone is 208.0° (corr.), regardless of the method of purification. The maximum yield is obtained when the concentration of phenylhydrazine is about 2.0 grams in 20 c.c. The efficiency of the reagent depends on the acidity, and is independent of the negative ion used. The maximum lies close to $P_{H^+}=4.7$, and is best secured with acetic acid and sodium acetate. Within fairly wide limits, the weight of sugar used has very little effect on the per-

centage yield of osazone. Maltose and dextrin retard the formation of glucosazone, and lactose retards it to a still greater extent, whilst starch has very little effect on its formation. The reaction is not complete in less than three hours. W. G.

The Oxidation of Maltose in Alkaline Solution by Hydrogen Peroxide and by Air. The Preparation and Study of Maltobionic Acid. J. W. E. GLATTFELD and MILTON T. HANKE (*J. Amer. Chem. Soc.*, 1918, **40**, 973—992. Compare Lewis and Buckborough, A., 1914, i, 1199).—The following products of the oxidation of maltose hydrate by hydrogen peroxide in the presence of potassium hydroxide were isolated or detected: formic acid, dextrose, *d*-erythrulactone, *d*-arabonic acid, glycollic, oxalic, and saccharinic acids. By oxidation with a rapid current of air in the presence of the alkali, glyceric acid was also produced.

Maltobionic acid was prepared by the oxidation of maltose by bromine in aqueous solution in the presence of lead carbonate at the ordinary temperature. The acid was isolated as its calcium salt, which had $[\alpha]_D^{20} + 97.5^\circ$. The free acid in aqueous solution had $[\alpha]_D^{20} + 98.3^\circ$. When hydrolysed with *N*/5-sulphuric acid, it gave gluconic acid and dextrose. It formed a *brucine* salt, m. p. 153° , $[\alpha]_D^{20} + 38.05^\circ$. W. G.

Direct Transformation of Secondary and Tertiary Amines into Nitriles. ALPHONSE MAILHE (*Compt. rend.*, 1918, **166**, 996—997).—The method used to transform di- and tri-*iso*-amylamine into *isovaleronitrile* by passing their vapours over finely divided nickel at 350 — 380° (compare A., 1917, i, 686) is shown to be generally applicable to secondary and tertiary aliphatic amines. Successful results were obtained with di- and tri-hexylamine, di- and tri-amylamine, di- and tri-butylamine, and di- and tri-propylamine. W. G.

Phosphotungstates of certain Bases and Amino-acids. JACK CECIL DRUMMOND (*Biochem. J.*, 1918, **12**, 5—24).—The phosphotungstates of bases and amino-acids yield figures on analysis which agree with the composition indicated by the formula $R_3H_3PO_4 \cdot 12WO_3 \cdot xH_2O$, where R is a univalent base. They are readily prepared by the addition of a very slight excess of 30% phosphotungstic acid solution to a solution of the base or its salt in 5% sulphuric acid. The best solvents for recrystallisation are water and 50% alcohol. *Lysine phosphotungstate* crystallises in anhydrous needles; crystalline *phosphotungstates of trimethylamine* (octahedra), *isobutylamine* (rhombic prisms), *isoamylamine*, *trisobutylamine*, *tripropylamine*, and *triisoamylamine* have also been obtained. *Putrescine* and *cadaverine phosphotungstates* closely resemble those of other bases in crystalline form and solubility. They readily dissolve in acetone, but in water they are all practically insoluble. *Phenylethylamine phosphotungstate* crystallises in yellow prisms, *p*-hydroxyphenylethylamine phospho-

tungstate in anhydrous, orange-red octahedra, β -iminoazolyethylamine and indole-ethylamine phosphotungstates in colourless prisms and brownish-purple needles respectively. The phosphotungstate of adenine crystallises in sulphur-yellow cubical or whetstone-shaped plates, of hypoxanthine and of xanthine in straw-coloured, cubical plates, and of uric acid in reddish-brown cubical plates. These purine phosphotungstates are characterised by very slight solubility, even in acetone. The phosphotungstates of betaine, stachydrine, nicotinic acid, choline, colamine (amino-ethyl alcohol), urea, and guanidine all crystallise in the form of rhombic prisms.

The study of the solubilities, crystalline forms, and other properties of these phosphotungstates indicates that they are not likely to be of much help in the identification of the parent bases, because of the lack of individual characteristics. The maximum precipitation usually occurs when a slight excess of phosphotungstic acid is added, and the final liquid contains 5% of sulphuric acid.

H. W. B.

Preparation and Attempts at Cyclisation of Dedimethylpiperidine [Dimethylamino- Δ^2 -pentene]. AMAND VALEUR and EMILE LUCE (*Bull. Soc. chim.*, 1918, [iv], 23, 182—185. Compare this vol., i, 102, 158).—Dimethylamino- Δ^2 -pentene may be prepared by shaking dimethylpiperidinium iodide in aqueous solution with moist silver oxide for three days. After filtering off the silver iodide formed, the alkaline liquid is concentrated under reduced pressure, and finally distilled. Attempts to produce ring formation by heating the base with sulphuric acid, by the action of hypochlorous acid, or by the action of hydriodic acid were not successful.

W. G.

Preparation of some Salts of β -Hydroxytrimethylenediglycine. HUGO KRAUSE (*Ber.*, 1918, 51, 542—554. Compare this vol., i, 156).—The following additional salts of β -hydroxytrimethylenediglycine, $\text{OH}\cdot\text{CH}(\text{CH}_2\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, have been prepared: potassium, $1\text{H}_2\text{O}$, and ammonium salts, very hygroscopic; a barium salt with $1\cdot5\text{H}_2\text{O}$, by double decomposition of the potassium salt and barium acetate in formalin solution; a comparatively stable zinc salt, $\text{C}_7\text{H}_{12}\text{O}_5\text{N}_2\text{Zn}\cdot\text{EtOH}\cdot\text{H}_2\text{O}$, precipitated by adding alcohol to a mixture of formalin and zinc glycine which had been left for ten hours at 50° ; another blue copper salt, $1\text{H}_2\text{O}$, which is extremely soluble, but decomposes in solution at below 50° , mainly according to the equation $\text{C}_7\text{H}_{12}\text{O}_5\text{N}_2\text{Cu} + 2\text{H}_2\text{O} = \text{Cu}(\text{C}_5\text{H}_8\text{O}_3\text{N})_2 + \text{MeOH}$, the metallic salt ($0\cdot5\text{H}_2\text{O}$) being precipitated as a crystalline, blue powder; mixtures of the mercurous and mercuric salts of the acid corresponding with the last copper salt (hydroxymethylglycine?) were obtained by the action of yellow mercuric oxide on β -hydroxytrimethylenediglycine.

Lead gives rise to some characteristic salts. When alcohol is added to a mixture of formalin and a concentrated solution of

lead glycine after leaving for ten hours at 50—55°, or to a mixture of the calcium salt and lead nitrate dissolved in formalin, methyl alcohol is expelled and the crystalline salt, $\text{Pb}(\text{C}_3\text{H}_5\text{O}_3\text{N})_2$, deposited. This becomes oily on kneading with water, and soon changes into the brilliant white basic salt, $2\text{PhX}_2\cdot\text{Ph}(\text{OH})\text{X}\cdot\text{H}_2\text{O}$ ($\text{X}=\text{C}_3\text{H}_5\text{O}_3\text{N}$). Solid lead glycine and formalin produce a third salt, $\text{Pb}(\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2)_2\text{O}$, which crystallises in glistening, microscopic spangles. J. C. W.

Dissociation Constants of some Higher Members of the α -Oximino-fatty Acids. CEDRIC STANTON HICKS (T., 1918, 113, 554—558).—Measurements have been made of the electrical conductivity of solutions of various α -oximino-fatty acids at dilutions varying from 16 to 256. The conductivity increases with time, but comparable values of the ionisation constants were obtained. The progress of the decomposition was investigated in the case of α -oximinoisovaleric acid by titration with alkali.

The results obtained are discussed in relation to the constitution of the acids, and it is suggested that the oximinic hydroxyl group acts as a negative substituent and not as an alcoholic group, as was implied by Hantzsch and Miolati. H. M. D.

The Amide Function. J. BOUGAULT (*Compt. rend.*, 1918, 166, 955—957).—From a comparison of the behaviour and mode of formation of amides with those of acyldisemicarbazinic acids and acyldihydroxamic acids (compare A., 1916, i, 764, 765; 1917, i, 417, 688, 694), the author considers that the constitution of amides is better represented by the formula $\text{R}\cdot\text{C}\begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NH} \end{smallmatrix}$ (acid type) than by the ordinary formula $\text{R}\cdot\text{CO}\cdot\text{NH}_2$ (basic type). This would explain the existence of metallic derivatives and of Pinier's imino-ethers. W. G.

The Preparation of Fumaronitrile. The Action of Hydroxylamine on Fumaronitrile. L. McMASTER and F. B. LANGRECK (*J. Amer. Chem. Soc.*, 1918, 40, 970—973).—The best yield (25%) of fumaronitrile was obtained by heating fumaramide with phosphoric oxide in a current of nitrogen at 170°. With hydroxylamine, the nitrile gave *fumaric acid diamidazime*, colourless needles, m. p. 212° (decomp.), together with a small amount of a yellow, cotton-like compound, m. p. 105° (decomp.), which rapidly darkens in the air. W. G.

The Stability of Cyclic Systems. J. BÖESEKEN [with (MILLER) M. DE GROOT and W. VAN LOOKEREN CAMPAGNE (*Rec. trav. chim.*, 1918, 37, 255—265)].—The mixture of cyclohexadienes prepared from 1:2-dibromocyclohexane is, like cyclohexene (compare Böeseken and Sillevius, A., 1914, i, 154), when passed as vapour, mixed with carbon dioxide, over reduced nickel at 180°, converted into benzene and cyclohexane in accordance with the equation $3\text{C}_6\text{H}_8=\text{C}_6\text{H}_{12}+2\text{C}_6\text{H}_6$.

An examination of the behaviour of *cyclobutane-1:1-dicarboxylic acid*, *cyclobutanecarboxylic acid* and its amide, and *cyclobutylamine* towards hydrogen in the presence of finely divided platinum shows that all these substances resist hydrogenation, the *cyclobutane* ring being, therefore, quite stable under these conditions.

W. G.

Catalytic Reduction of Organic Halogen Compounds.

KARL W. ROSENMUND and FRITZ ZETZSCHE (*Ber.*, 1918, 51, 578—585).—The removal of halogen from organic compounds by the action of hydrogen in the presence of a catalyst has been the subject of a number of papers in recent years, and has actually been developed into methods for estimating halogens (see Borsche and Heimbürger, A., 1915, i, 527, 640; Busch and Stöve, A., 1916, ii, 534; Kelber, A., 1917, ii, 215). The authors have also been engaged on this work, and now make a useful summary of their results.

They find that colloidal palladium protected by gum arabic, or palladinised barium sulphate is an efficient catalyst, and that it is usually advisable to have an alkali present to neutralise the halogen hydracid as it is formed. Many substances react even if merely suspended in aqueous alkalis. In the case of halogen derivatives of ethylenic compounds, the halogen may sometimes be removed without saturating the double linking or the halogen derivative of the saturated compound may be formed. Frequently, the reaction proceeds smoothly to hydrogenation and removal of halogen. In the case of dihalogen compounds, it is apparently impossible to obtain mono-derivatives.

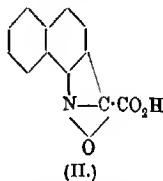
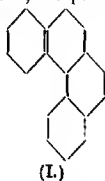
As illustrations, the following reductions are described: bromobenzene to benzene; *o*-bromobenzoic acid to benzoic acid; 1:4-bromonitrobenzene to aniline; chlorocaffeine to caffeine; chlorocrotonic acid to crotonic acid; *o*-chlorocinnamic acid to β -phenylpropionic acid; dibromosuccinic acid to succinic acid. J. C. W.

***p*-Cymene. I. Nitration. Mononitrocymene.** C. E. ANDREWS (*J. Ind. Eng. Chem.*, 1918, 10, 453—456).—*p*-Cymene was nitrated by mixing it with an equal weight of sulphuric acid, cooling to 0°, and adding a mixture of nitric and sulphuric acids, the temperature being kept at 0°, or lower. The yield of mononitrocymene was 85%; small quantities of *p*-toluic acid and *p*-tolyl methyl ketone were formed during the nitration. The nitrocymene was reduced to the corresponding amine, which (and also the nitro-compound) consisted of the 1:2:4-isomeride. [See, further, *J. Soc. Chem. Ind.*, 1918, August.] W. P. S.

Naphthylacetic Acids. II. 3:4-Benzphenanthrene. FRITZ MAVER and TRUDI OPPENHEIMER (*Ber.*, 1918, 51, 510—516).—Weitzenböck and Lieh briefly outlined the most rational method for the synthesis of 3:4-benzphenanthrene from β -naphthylacetic acid (A., 1912, i, 548), but this parent substance has since become

more readily available (A., 1916, i, 816), and the synthesis has now been examined in detail.

Sodium β -naphthylacetate, *o*-nitrobenzaldehyde, and acetic anhydride are heated for some hours at 120–130°, the *o*-nitro- α -2-naphthylcinnamic acid, m. p. 177–178°, so formed is reduced by ferrous sulphate and ammonia to the *o*-amino-acid, m. p. 191–192°, which is diazotised and shaken with copper powder, when 3:4-benzphenanthrene-1-carboxylic acid, m. p. 218°, is produced. When distilled at 400° in a current of carbon dioxide, this acid gives a poor yield of 3:4-benzphenanthrene (I), crystallising in needles or leaflets, m. p. 158–160°, and forming a red *picrate*, m. p. 140–141°.



Potassium 1-nitro-2-naphthylacetate loses water when heated with acetic anhydride and zinc chloride, and cannot, therefore, be made to condense with benzaldehyde. The product is *naphthanthroxanic acid* (II), m. p. 218°.

In the above synthesis, there is a possibility of the condensation of the *o*-amino- α -2-naphthylcinnamic acid leading alternatively to a naphthanthracenecarboxylic acid. Small quantities of by-products are, indeed, formed, but it is difficult to isolate sufficient to ascribe any definite constitution to them.

J. C. W.

Some Halogen Derivatives of Aromatic Amines and their Analysis. I. F. B. DAINS, T. H. VAUGHAN, and W. M. JANNEY

(*J. Amer. Chem. Soc.*, 1918, **40**, 930–936. Compare Wheeler, A., 1910, i, 17, 19, 662; 1911, i, 27).—Iodine reacts with chloro- and bromo-anilines to give iodo-derivatives. Thus *p*-bromoaniline gives 4-bromo-2-iodoaniline, m. p. 71°, yielding a *hydrochloride*, m. p. 205–206°; an *acetyl* derivative, m. p. 148°; a *benzoyl* derivative, m. p. 152°; 4-bromo-2-iododiphenylthiocarbamide, m. p. 167°; 4-bromo-2-iodophenylallylthiocarbamide, m. p. 177°; 4-bromo-2-iodophenylcarbamide, m. p. 167°; *anisylidene*-4-bromo-2-iodoaniline, m. p. 118°; *cinnamylidene*-4-bromo-2-iodoaniline, m. p. 96°; *piperonylidene*-4-bromo-2-iodoaniline, m. p. 120°; and *o*-nitrobenzylidene-4-bromo-2-iodoaniline, m. p. 159°. If in the above preparation 2 mols. of iodine are used, the product is a mixture of 4-bromo-2-iodoaniline and 4-bromo-2:6-di-iodoaniline, m. p. 148°.

From *m*-bromoaniline, a 3-bromoiodoaniline, m. p. 56°, giving a *hydrochloride*, m. p. 192°, and an *acetyl* derivative, m. p. 199°, is obtained in which the position of the entrant iodine atom has not been definitely ascertained.

p-Chloroaniline yields 4-chloro-2(?)-iodoaniline, m. p. 46°, giving a *hydrochloride*, m. p. 202°, an *acetyl* derivative, m. p. 150°, and a *benzoyl* derivative, m. p. 145°. 4-Chloro-*di*-iodoaniline, m. p. 129°, giving a *benzoyl* derivative, m. p. 205°, was also prepared.

o-Chloroaniline yielded 2-chloro-4-iodoaniline (compare Werner and Caldwell, T., 1907, 91, 246). It gave a *hydrochloride*, m. p. 190°, a *benzanilide*, m. p. 165°, and a *phenylcarbamide*, m. p. 175°.

m-Chloroaniline yielded with iodine 3-chloro-4-iodoaniline, m. p. 65°, giving a *hydrochloride*, m. p. 180°, an *acetyl* derivative, m. p. 170°, and a *benzoyl* derivative, m. p. 144°. The base when diazotised and treated with potassium iodide gave 2-chloro-1:4-di-iodobenzene, m. p. 51°, similar to that obtained in the same way from 2-chloro-4-iodoaniline.

2:4-Dichloroaniline only undergoes iodination with difficulty, yielding a small amount of 2:4-dichloro-6(?)iodoaniline, m. p. 85°, giving a *hydrochloride*, m. p. 180°.

In the majority of the above cases the yields were good, but if the hydrogen of the ring is replaced by two or three methyl groups or by a methoxy-, ethoxy-, or acetylamino-group, the yield of the iodo-derivative was poor, or only resinous products were obtained. The same is true of the methyl- and dimethyl-anilines. Thus ψ -cumidine only gave a small yield of 2-iodo-3:4:6-trimethylaniline, m. p. 93°. *o*-Anisidine gave 4(?)iodo-2-methoxyaniline, m. p. 49°, giving a *hydrochloride*, m. p. 180°, and an *acetyl* derivative, m. p. 176°. *p*-Anisidine only gave a black, waxy, resinous substance, and acetyl-*p*-phenylenediamine behaved in a similar manner.

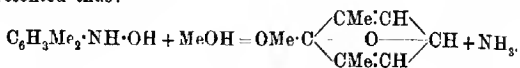
For the estimation of the halogens in these and similar halogen derivatives, the authors advocate a slight modification of Chablay's method (compare A., 1907, ii, 195), the compound being decomposed by sodium in liquid ammonia. [For details, see *J. Soc. Chem. Ind.*, August.] W. G.

Phenylcarbamates of Terpenic Alcohols and Phenols.

F. WEERUIZEN (*Rec. trav. chim.*, 1918, 37, 266—269).—Phenylcarbamates may be readily obtained in a crystalline state by boiling the alcohol or phenol with the requisite amount of phenylcarbimide in light petroleum (b. p. 170—200°) for a half to one hour. In this way, excellent results were obtained with the three cresols, thymol, menthol, borneol, and eugenol, but good results were not obtained with geraniol or linalool. Camphor may be separated from borneol by this method, the unattacked camphor remaining in solution in the solvent on cooling, whilst the bornyl phenylcarbamate crystallises out. W. G.

Peculiar Action of Methyl Alcohol containing Sulphuric Acid on a β -Arylhydroxylamine. EUG. BAMBERGER (*Ber.*, 1918, 51, 629—634).—When *m*-2-xylylhydroxylamine is left with a mixture of methyl alcohol and a little concentrated sulphuric acid,

the main product is 5-methoxy-*m*-2-xylydine (A., 1903, i, 624), but this is accompanied by a small quantity of a neutral substance, ammonia being formed as well. The isolation of this compound in a yield of about 4.5% is now described. It is referred to as an "*oxide*," and it crystallises from acetone in glassy prisms, *m. p.* 139–140°, contains a methoxyl group but no hydroxyl group, and changes into formaldehyde and *m*-2-xylenol when heated at 250–260°. Its formation and constitution are provisionally represented thus:



J. C. W.

Acetylation of β -Phenylhydroxylamine. EUG. BAMBERGER (*Ber.*, 1918, 51, 636–640).—Phenylhydroxylamine can be readily converted into its *N*-acetyl derivative by means of acetic anhydride, and the reaction can be adapted to the detection of the base, as follows. A few mg. of the substance are dissolved in cold water, three separate drops of acetic anhydride are added at half-minute intervals, with shaking, followed by a drop of very dilute ferric chloride, when the violet-red colour, changing into grey and then bluish-green, characteristic of the acetyl derivative, develops (see A., 1902, i, 539).

For quantitative purposes, thioacetic acid is a better acetylating agent. The reagents are mixed in dry alcohol, left for a few days, when the solvent is evaporated, the residue rendered alkaline and shaken with ether to remove by-products, and then the solution is acidified and extracted with ether. *N*-Acetylphenylhydroxylamine (*ibid.*) is soluble in ammonia solution and in 2*N*-sodium carbonate.

Diacetylphenylhydroxylamine, $\text{C}_6\text{H}_5\cdot\text{NAc}\cdot\text{OAc}$, glassy prisms, *m. p.* 43°, is the product when the base is left with an excess of acetic anhydride. J. C. W.

The Electrolytic Reduction of *p*-Aminophenol. T. SUGAI (*J. Chem. Ind., Tokyo*, 1918, 21, 117–136).—The principal product of the electrolytic reduction of nitrobenzene in presence of strong sulphuric acid with platinum electrodes is *p*-aminophenol; the use of a carbon cathode is permissible. The concentration of the sulphuric acid electrolyte must not exceed 80%, otherwise there will be a loss of aminophenol by sulphonation. The quantity of sulphuric acid should be five times that of the nitrobenzene; the temperature must be kept at about 80°; a higher temperature induces sulphonation. The current density is 8–9 amperes per sq. dm., and the *E.M.F.* 6–8 volts. Vigorous agitation of the electrolyte is most important for obtaining a good current efficiency. The cathode chamber must be kept closed to prevent loss of nitrobenzene by volatilisation. Under these conditions, the author obtained 80 grams of crude *p*-aminophenol sulphate from 100

grams of commercial nitrobenzene, yielding 38 grams of free base, or 43% of the theoretical quantity. J. F. B.

β -Cholesterol, some of its Derivatives and Oxidation Products. GEORGE WILLIAM ELLIS and JOHN ADDYMAN GARDNER (*Biochem. J.*, 1918, 12, 72—80).—The following derivatives of β -cholesterol have been prepared: *chloroacetate*, $C_{26}H_{48}O_2Cl$, by the action of chloroacetyl chloride in chloroform solution, glistening plates from a mixture of chloroform and ethyl acetate, m. p. 178—179°; *benzoate*, $C_{34}H_{62}O_2$, by the action of benzoyl chloride in pyridine solution, crystallising from ethyl acetate in small plates. It melts at 155° with brilliant fluorescence during the rise of temperature from about 138° to 155°, $[\alpha]_D^{25} + 23.3^\circ$ in chloroform solution; *stearate*, $C_{46}H_{82}O_2$, by boiling with stearyl chloride in chloroform solution, flaky crystals from a mixture of alcohol and chloroform, m. p. 100°, $[\alpha]_D^{25} + 18.4^\circ$ in ether solution.

On oxidation, β -cholesterol yields β -cholestanone (Diels and Abderhalden, A., 1906, i, 272), which on further oxidation with ammonium persulphate has been found to give a number of lactones of the formula $C_{27}H_{46}O_2$, of which three have been isolated in a more or less pure state and found to melt at 98—100°, 159—161°, and 201—202° respectively. These substances are different, however, from those prepared in a similar manner from coprostanone (Gardner and Goddard, A., 1914, i, 169). H. W. B.

Preparation of Benzoic Acid. WESTON CHEMICAL CO., and J. SAVAGE (Brit. Pat. 116348).—Toluene is converted into benzoyl chloride, with traces of benzylidene chloride, by chlorination at the boiling point; the benzyl chloride is converted into benzyl alcohol by boiling with sodium hydroxide solution or milk of lime, and the alcohol is oxidised to alkali benzoate by means of a hypochlorite in presence of alkali. A. S.

Catalytic Action of Colloidal Metals of the Platinum Group. XVI. Partial Reduction of Phenylpropionic Acid with Colloidal Platinum. C. PAAL and ANTON SCHWARZ (*Ber.*, 1918, 51, 640—643).—It has already been shown that the hydrogenation of phenylpropionic acid and acetylene can be so controlled under certain conditions, using colloidal palladium as the catalyst, that the corresponding ethylenic compounds are the main products (A., 1909, i, 926; 1915, i, 113). In the case of acetylene, it has also been shown that colloidal platinum is less efficient, and that a mixture of ethylene, ethane, and unreduced acetylene is generally obtained (A., 1915, i, 765). The hydrogenation of phenylpropionic acid by means of colloidal platinum has now been studied. The yield of malenoid forms of cinnamic acid is found to be much less than when palladium is used, but no β -phenylpropionic acid could be detected under the conditions employed. The deficiency is largely due to the formation of indefinite by-products. J. C. W.

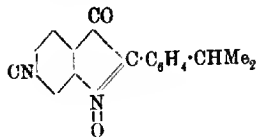
The Border-line between Isomerism and Polymorphism.
III. PAUL PREIFFER [with J. KLINKERT] (*Ber.*, 1918, 51, 554—567. Compare A., 1916, i, 24; 1917, i, 140).—It has been shown that certain nitromethoxystilbenes exhibit a kind of isomerism which is termed "cryptoisomerism," and this communication records some further experiments designed to find what conditions are necessary for the display of this phenomenon. It is shown, on the one hand, that the nitro-group may be in the ortho- or para-position in the one benzene nucleus (the question of the meta-position is not discussed), and that, on the other hand, a hydroxyl or methoxyl group, but not alkyl or acyloxyl, must be in the para-, but not the ortho-, position in the other benzene nucleus. That is, besides the chromophores, nitro-group and ethylene linking, there must be an auxochrome.

4-Nitro-3-cyanostilbene, obtained by heating *p*-nitro-*m*-toluonitrile with benzaldehyde and a few drops of piperidine at 140°, crystallises in golden-yellow, flat needles, m. p. 187°, and may be hydrolysed by boiling with aqueous-alcoholic potassium hydroxide to 4-nitrostilbene-3-carboxylic acid, pale yellow, glistening leaflets, m. p. 203°. 4-Nitro-3-cyano-4'-isopropylstilbene, from cuminaldehyde, forms golden-yellow leaflets, m. p. 132—133°, and 4-nitro-3-cyano-4'-methoxystilbene, from anisaldehyde, crystallises in brownish-orange, glistening leaflets, m. p. 161°.

p-Nitro-*o*-toluonitrile gives rise to 4-nitro-2-cyano-4'-isopropylstilbene, orange-yellow needles, m. p. 195°, and 4-nitro-2-cyano-4'-hydroxystilbene (*ibid.*, 140). The latter crystallises from glacial acetic acid in orange-yellow needles, m. p. 226°, but if the solution is poured into water, a pure yellow variety is deposited, which becomes permanently orange-yellow on heating at about 200°. It also forms an acetate (*ibid.*) and a benzoate, glistening, yellow, flat needles, m. p. 178°.

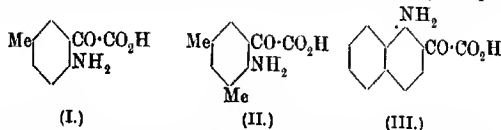
o-Nitro-*p*-toluonitrile is the parent of the following derivatives: 2-Nitro-4-cyano-4'-isopropylstilbene, which crystallises with 0.5 mol. AcOH in flat, yellow needles, m. p. 134—138° (142° when deprived of crystal solvent). 2-Nitro-4-cyano-4'-hydroxystilbene, which exists in two forms, an orange-yellow, giving a pale orange-yellow hydrate, and an orange-red, giving an orange solvate with 1AcOH; the two forms exhibit the same colour in any particular solvent, but the shades vary with the solvent; they both have the same colour at 210° and melt at 230—231°; the acetate has m. p. 225°, not 186° (*ibid.*). 2-Nitro-4-cyano-4'-hydroxy-3'-methoxystilbene, from vanillin, forms glistening, orange needles, m. p. 207°, and its acetate, yellow leaflets, m. p. 170°.

The above 2-nitro-4-cyano-4'-isopropylstilbene yields a mixture of chlorides (m. p. 120—125° and 150°) when treated with chlorine in carbon disulphide. When a solution of these in pyridine is exposed to sunlight, 6-cyano-4'-isopropyl-2-



phenylisatogen (annexed formula) is deposited, in orange-red needles, m. p. 220° (compare A., 1916, i, 327). J. C. W.

The Isatoic Acids. J. MARTINET (*Compt. rend.*, 1918, **166**, 952—955).—Three isatoic acids have been obtained by dissolving the corresponding isatins in a known volume of standard potassium hydroxide, and, after the liquid has turned yellow, cooling and adding the calculated quantity of hydrochloric acid. The voluminous precipitate is collected and dried rapidly over phosphoric oxide. In this way, 5-methylisatin yielded 5-methylisatoic acid (6-amino-m-tolylglyoxylic acid) (formula I), m. p. 132° ; 5:7-dimethylisatin gave 5:7-dimethylisatoic acid [2-amino-3:5-dimethylphenylglyoxylic acid] (formula II), an orange-yellow, crystalline powder, m. p. 215° ; α -naphthisatin gave α -naphthisatoic acid [α -aminonaphthyl- β -glyoxylic acid] (formula III), m. p. 187° .



These acids give citron-yellow potassium and barium salts, orange-yellow lead salts, red copper salts, and pale yellow silver salts.

W. G.

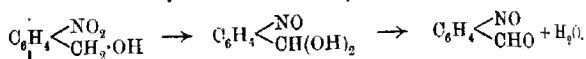
Tetraiodophenolphthalein and Tetrachlorotetraiodophenolphthalein and some of their Derivatives. W. R. ORNDORFF and S. A. MAHOON (*J. Amer. Chem. Soc.*, 1918, **40**, 937—955).—Tetraiodophenolphthalein was prepared by the method of Classen and Löb (compare A., 1895, i, 539) with slight modifications, and was finally obtained in the form of colourless needles decomposing at 270 — 272° . Contrary to the opinion of these two authors, the corresponding free carbinolcarboxylic acid could not be obtained, although its potassium and disodium salts were prepared. These salts when heated gave the corresponding salts of tetraiodophenolphthalein. When dry ammonia was passed over the phthalein, a tetra-ammonia salt, $C_{20}H_{10}O_4I_4 \cdot 4NH_3$, was obtained. Tetraiodophenolphthalein gave a diacetate, m. p. 246° , a dibenzoate, m. p. 298° , and an oxime, m. p. 170° .

By the iodination of tetrachlorophenolphthalein in alkaline solution, tetrachlorotetraiodophenolphthalein, $\begin{matrix} C_6Cl_4 \\ CO-O \end{matrix} > C(C_6H_2I_2 \cdot OH)_2$, decomposing at 240 — 244° , was obtained, which gave a diacetate, m. p. 262° , a dibenzoate, m. p. 205° , and with dry ammonia a tetra-ammonia salt.

A study of the visible and ultra-violet absorption spectra of these and other phenolphthalein derivatives showed that neutral alcoholic solutions of these phthaleins have absorption spectra of the same type, but that the type changes when the solution becomes alkaline, the characteristic spectrum of the alkaline solutions having

three absorption bands, one at $\lambda=1600-1800$, the second at $\lambda=2500-2700$, and the third at $\lambda=3200-3600$. The magnitude of the first two bands varies greatly with the phthalein. Bromine and iodine in the phenol residues shift all bands towards lower frequencies. Chlorine in the phthalic residue shifts the visible band in the same direction, but the two ultra-violet bands in the opposite direction. The shift increases with the mass of the substituent. W. G.

Anthranil. XXI. Photochemical Formation of *o*-Nitrosobenzaldehyde. EUG. BAMBERGER (*Ber.*, 1918, 51, 606-612).—Sachs and Hilpert (*A.*, 1904, i, 876) exposed a benzene solution of *o*-nitrosobenzyl alcohol to the light, in the hope of obtaining *o*-nitrosobenzaldehyde, according to the scheme:

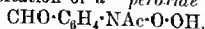


During 1909 and 1910, the author exposed an ethereal solution to the sunlight for about 830 hours at Davos Platz, and now describes the examination of the product. He finds that *o*-nitrosobenzaldehyde is formed, but that it largely suffers oxidation, on the one hand, to *o*-nitrosobenzaldehyde and *o*-nitrobenzoic acid, and reduction, on the other hand, to *o*-nitrosobenzyl alcohol, whence anthranil is formed, and probably *oo'*-azoxybenzaldehyde, whence indazolybenzoic acid and its lactone. J. C. W.

Anthranil. XXII. *N*-Acetyl-*o*-hydroxylaminobenzaldehyde. EUG. BAMBERGER (*Ber.*, 1918, 51, 613-629).—The discovery that anthranil is the anhydride of *o*-hydroxylaminobenzaldehyde has naturally led the author to attempt to isolate this compound, but so far it has only been obtained in the form of a very impure, dilute solution (*A.*, 1904, i, 94). The production of the *N*-acetyl derivative is now described, and with this the research is broken off.

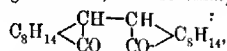
"Agnobenzaldehyde," the primary reduction product of *o*-nitrosobenzaldehyde (*A.*, 1907, i, 163), is treated with acetic anhydride, added drop by drop, at 0°, and thus converted into *o*-nitrosobenzaldehyde and *N*-acetyl-*o*-hydroxylaminobenzaldehyde, $\text{CHO}\cdot\text{C}_6\text{H}_4\cdot\text{NAc}\cdot\text{OH}$, which crystallises from slowly cooling benzene in glassy, triclinic prisms melting at 132° if plunged in a bath at 110° and then heated further, but changing slowly at about 125° into acetylantbranilic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, thus becoming solid again. The compound dissolves in concentrated sulphuric acid with lemon-yellow colour, anthranil being deposited on dilution. An aqueous suspension gives a deep violet-red colour with ferric chloride. It is soluble in alkali hydroxides or carbonates or aqueous ammonia with lemon- to orange-yellow colour, but the solutions suffer obscure changes when kept. The *phenylhydrazone* forms golden-yellow, silky needles, m. p. 120-120.5° (180-181° on one occasion), and dissolves in sodium hydroxide with magenta

colour. When a solution of bleaching powder is slowly added to a cold, supersaturated solution of the aldehyde in water, *o*-nitrosobenzaldehyde is precipitated, the yield being as high as 85%. *o*-Nitrobenzaldehyde is also formed if too much hypochlorite is used, whilst the addition of perhydrol to a solution in glacial acetic acid causes the precipitation of a "peroxide" (?),



in satiny, flat needles, m. p. 110.5–111°, which gives the peroxide reaction with titanium dioxide in sulphuric acid. J. C. W.

Bornylenecamphor and a New Dicumphor, *iso*Dicumphor. MARCEL GUERBET (*Compt. rend.*, 1918, 166, 1049–1052).—When camphor is heated with sodium methoxide in methyl-alcoholic solution, the main product is not bornylenecamphor, only a trace of this compound being obtained, but *isodicumphor*,



m. p. 196°, $[\alpha]_D^{18} + 64.54'$ (in alcohol).

At 250° it is slowly converted into camphor. It yields a *monoxime*, m. p. 159–160°, and a *diorime*, m. p. 235°. On bromination, it gives *bromoisodicumphor*, $\text{C}_{20}\text{H}_{30}\text{O}_2\text{Br}$, m. p. 161°, and *dibromoisodicumphor*, m. p. 132°. When oxidised by dilute nitric acid, it yields camphoric acid. W. G.

Nomenclature of Hydrocyanic Glucosides of the Amygdalin Group. EM. BOURQUELOT (*J. Pharm. Chim.*, 1918, [vii], 17, 359–361).—When hydrolysed with hot concentrated hydrochloric acid, prunasin yields *l*-phenylglycollic acid, prulaurasin gives inactive phenylglycollic acid, and sambunigrin (A., 1905, i, 912) *d*-phenylglycollic acid. Under the same conditions, amygdalin gives the *l*-acid, *iso*amygdalin the inactive acid, and *d*-amygdalin the *d*-acid. The relations of these glucosides is therefore as follows:

Monoglucosides, $\text{C}_{14}\text{H}_{17}\text{O}_4\text{N}$

Prunasin
Prulaurasin
Sambunigrin

Diglucosides, $\text{C}_{20}\text{H}_{27}\text{O}_{11}\text{N}$.

l-Amygdalin or gluco-prunasin
*iso*Amygdalin or gluco-prulaurasin.
d-Amygdalin or gluco-sambunigrin.

The diglucosides may be converted into the corresponding monoglucosides by the action of dry bottom-fermentation yeast.

W. P. S.

A New Group of cycloPropane Derivatives. I. Action of Phenylacetyl Haloids on 3-Acylcoumarins in the Presence of Sodium Alkylloxides. OSKAR WIDMAN (*Ber.*, 1918, 51, 533–541).

—When 3-acetylcoumarin and *o*-halogenoacetophenones are mixed in cold alcohol and treated with one atomic proportion of sodium ethoxide solution, two products are obtained which are indifferent towards permanganate, the ethylene linking in the coumarin ring being saturated by the addition of the phenacylidene residue,

cyclopropane derivatives resulting. The chief product is 3-acetyl-3:4-phenacylidene coumarin, $\begin{matrix} \text{C}_6\text{H}_4\text{-CH} \\ \text{O-CO-CAc} \end{matrix} > \text{CHBz}$, which crystallises in silky needles, m. p. 184°, and the other compound, which is the more soluble in alcohol, is ethyl α -acetyl- $\alpha\beta$ -phenacylidene coumarate [ethyl 1-acetyl-2-benzoyl-3- α -hydroxyphenylcyclopropane-1-carboxylate], $\begin{matrix} \text{CAc-CO}_2\text{Et} \\ \text{CH-C}_6\text{H}_4\text{-OH} \end{matrix} > \text{CHBz}$. This crystallises in brilliant, quadratic prisms, m. p. 117°, and forms an acetate, lustrous octahedra, m. p. 89°. The condensation must proceed most readily, for the ω -halogenoacetophenones give rise to the 2-halogeno-3:4-oxido-3:5-diphenyltetrahydrofurans when left with sodium alkyl oxides alone (A., 1913, i, 1219), and no trace of these compounds is found in the present instance.

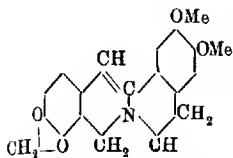
Similar compounds are produced by other 3-acylcoumarins. Thus 3-propionylcoumarin, very long, silky needles, m. p. 134° (from salicylaldehyde and ethyl propionylacetate) gives rise to 3-propionyl-3:4-phenacylidene coumarin, needles, m. p. 157—158°, and ethyl α -propionyl- $\alpha\beta$ -phenacylidene coumarate, prisms or irregular hexagonal tablets, m. p. 109—110°. 3-Benzoylcoumarin, m. p. 135—136° (compare Knoevenagel and Arnot, A., 1905, i, 65), forms 3-benzoyl-3:4-phenacylidene coumarin, tablets, m. p. 189—190°, there being also a suggestion of *cis-trans*-isomerism in this case. Ethyl coumarin-3-carboxylate forms ethyl 3:4-phenacylidene coumarin-3-carboxylate, flat needles, m. p. 176—177°; methyl coumarin-3-carboxylate, m. p. 116—117° (from methyl malonate and salicylaldehyde), yields the corresponding methyl ester, m. p. 183°, mixed with "methyl ethyl $\alpha\beta$ -phenacylidene salicylidene malonate" [methyl ethyl 2-benzoyl-3- α -hydroxyphenylcyclopropane-

1:1-dicarboxylate], $\begin{matrix} \text{CO}_2\text{Me} \\ \text{CO}_2\text{Et} \end{matrix} > \begin{matrix} \text{CHBz} \\ \text{CH-C}_6\text{H}_4\text{-OH} \end{matrix} \text{H}_2\text{O}$, this being the more soluble in alcohol, and crystallising in glistening rhombohedra, m. p. 96°. The 3:4-phenacylidene coumarin-3-carboxylates are hydrolysed by 4% sodium hydroxide to salicylaldehyde, phenacylmalonic acid, $\text{CH}_2\text{Bz-CH}(\text{CO}_2\text{H})_2$, and α -hydroxy- γ -benzoyl- α - α -hydroxyphenylpropane- $\beta\beta$ -dicarboxylic acid,

$\text{OH-C}_6\text{H}_4\text{-CH}(\text{OH})\text{-C}(\text{CO}_2\text{H})_2\text{-CH}_2\text{Bz}$, short prisms, m. p. 126—128° (decomp.). 3-Cyanocoumarin also condenses with ω -bromoacetophenone, yielding 3-cyano-3:4-phenacylidene coumarin, in slender needles, m. p. 218°. J. C. W.

epiBerberine. WILLIAM HENRY PERKIN, jun. (T., 1918, 113, 492—522).—An attempt to prepare *epiberberinium* hydroxide and to compare its properties and those of its salts with those of berberinium hydroxide and its salts (compare T., 1916, 109, 833). Attempts to demethylate cryptopine by the method of Diels and Fischer as applied to codeine (compare A., 1914, i, 989) were not successful. It was noticed, however, that many methochlorides, such as 6:7-dimethoxy-2-methyltetrahydroisoquinoline, decompose

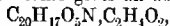
at their melting points, giving off methyl chloride. β -Tetrahydroanhydroberberine methochloride (Pyman, T., 1913, **103**, 828) in this way loses its methyl chloride. *iso*Cryptopine chloride when heated in small quantities under diminished pressure decomposes at 260°, giving methyl chloride and *dihydroanhydroepiberberine*



(annexed formula), crystallising in iridescent, golden, monoclinic plates [$a:b:c=1.163:1.0:0.995$; $\beta=97^\circ 15'$], m. p. 172—174°. It gives a *hydrochloride*, $C_{20}H_{18}O_4N.HCl.3H_2O$, a *hydrobromide*, a *methosulphate*, m. p. 260° (decomp.), and a *methiodide*, m. p. 245° (decomp.). The methosulphate when boiled with methyl-alcoholic potassium hydroxide yields anhydrocryptopine (T., 1916, **109**, 975). *Tetrahydroanhydroepiberberine*, $C_{20}H_{21}O_4N$, m. p. 170—171°, is obtained either by the action of heat on *isodihydrocryptopine* α -chloride or β -chloride, or by the reduction of *dihydroanhydroepiberberine* with zinc or tin and hydrochloric acid. It is a strong base, and gives a *hydrochloride*, a *sulphate*, a *nitrate*, and a *methosulphate*, m. p. 255—260° (decomp.), which is decomposed by boiling with methyl-alcoholic potassium hydroxide, giving anhydrodihydrocryptopine.

When *dihydroanhydroepiberberine* or the tetrahydro-derivative is acted on by oxidising agents, such as bromine, iodine, or dilute nitric acid, or preferably by mercuric acetate in acetic acid solution, various, deep orange salts of *epiberberine* are obtained by suitable subsequent treatment. In this way, the author has prepared *epiberberinium chloride*, $C_{20}H_{18}O_4NCl.4H_2O$, which gives a *platinichloride*, the *sulphate*, the *iodide*, and the *picate*, m. p. 222°.

*epi*Berberinium sulphate is decomposed by aqueous sodium hydroxide in the same manner as is berberinium sulphate, and yields *oxyepiberberine*, $C_{20}H_{17}O_5N$, m. p. 240—241°, and *dihydroanhydroepiberberine*. *Oxyepiberberine* gives an *acetate*,



which is dissociated by water or heat. By the action of hydrochloric acid, *oxyepiberberine* is converted into *isooxyepiberberine*, needles. Although it was not found possible to isolate *epiberberine* itself, its O-methyl and O-ethyl derivatives have been obtained in a pure condition by the action of sodium methoxide and ethoxide respectively on *epiberberinium chloride*. *O-Methylepiberberine* separates in golden prisms, m. p. 150—152° (decomp.), and *O-ethylepiberberine*, $C_{20}H_{19}O_4(OEt)N$, in needles, m. p. 135—136° (decomp.). Both these compounds dissolve readily in boiling acetone, and from the solution, on cooling, *anhydroepiberberineacetone*, $C_{20}H_{17}O_4N.C_3H_6O$, m. p. 162°, separates. The author discusses fully the nomenclature of berberine and its salts. For experimental details, see the original.

W. G.

Metallic Derivatives of Alkaloids. JITENDRA NATH RAKSHIT (T., 1918, 113, 466—471).—Sodium and potassium derivatives of codeine and narcotine and the sodium derivative of cotarnine were obtained by boiling the alkaloids with the respective metals in benzene. *Sodium codeine*, $C_{18}H_{20}O_3NNa$, is a brownish-yellow powder which, in aqueous solution, does not give any precipitate with Mayer's reagent until the mixture is acidified. *Potassium codeine*, $C_{18}H_{20}O_3NK$, forms reddish-brown crystals. *Sodium narcotine*, $C_{22}H_{22}O_7NNa$, was obtained as a reddish-yellow powder, which is decomposed in aqueous solution by carbon dioxide, narcotine being liberated. *Dipotassium narcotine*, $C_{22}H_{21}O_7NK_2$, is a bright yellow, crystalline powder. *Tetrasodium cotarnine*, $C_{12}H_{11}O_4NNa_4$, is a hygroscopic, bright yellow, crystalline powder. *Calcium morphinate*, $(C_{17}H_{18}O_3N)_2Ca$, was obtained by triturating morphine with calcium hydroxide in the presence of alcohol as a brown, non-deliquescent powder, which is readily decomposed by carbon dioxide. W. G.

The Presence of a Fixed Alkaloid in the Common Broom. AMAND VALEUR (*Compt. rend.*, 1918, 167, 26—28).—From the mother liquors resulting from the crystallisation of sparteine sulphate as prepared from *Sarothamnus scoparius*, the author has isolated another alkaloid, *sarothamnine*, which readily forms crystalline compounds with various solvents. Thus *sarothamnine-chloroform*, $C_{15}H_{21}N_3 \cdot \frac{1}{2}CHCl_3$, has m. p. 127° and $[\alpha]_D - 38.7^\circ$; *sarothamnine-ethyl alcohol*, $C_{15}H_{21}N_3 \cdot \frac{1}{2}EtOH$, has m. p. 90° , $[\alpha]_D - 25.6^\circ$. It unites similarly with methyl alcohol and benzene. The alkaloid is unsaturated, since it reduces aqueous potassium permanganate in the cold. W. G.

Pyridine Derivatives from $\alpha\beta$ -Dichloroethyl Ether and Ethyl β -Aminocrotonate, and related Amino-compounds. II. ERICH BENARY (*Ber.*, 1918, 51, 567—577. Compare A., 1911, i, 320).—The action of various agents on the 4-chloromethylpyridine derivatives described in the earlier paper, and the production of similar esters from acetylacetoneamine and benzoylacetoneamine are dealt with in this paper.

The reaction between $\alpha\beta$ -dichloroethyl ether and ethyl β -aminocrotonate, whereby ethyl 2:6-dimethyl-4-chloromethyl-1:4-dihydropyridine-3:5-dicarboxylate is formed, is best effected in the presence of dilute aqueous ammonia. The ester reacts with potassium hydrosulphide to form the 4-thiolmethyl derivative, which crystallises in slender needles, m. p. $86-87^\circ$, and with bromine to give a *dibromo-dibromide*, pale yellow needles, m. p. $109-110^\circ$, which may be oxidised by pure nitric acid to the corresponding *ethyl dibromo-2:6-dimethyl-4-chloromethylpyridine-3:5-dicarboxylate dibromide*, $C_{14}H_{16}O_4NClBr_4$, m. p. $114-115^\circ$.

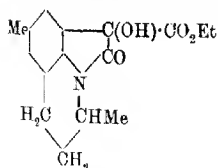
More important results may be obtained with ethyl 2:6-dimethyl-4-chloro-(or iodo-)methylpyridine-3:5-dicarboxylate. Hydrolysis with boiling 10% sodium hydroxide gives rise to the *lactone* of

2:6-dimethyl-4-hydroxymethylpyridine-3:5-dicarboxylic acid, hard crystals, m. p. 213°. With alcoholic ammonia at 100—110°, the product is the lactam of ethyl hydrogen 2:6-dimethyl-4-aminomethylpyridine-3:5-dicarboxylate, needles, m. p. 168—169°, which may be hydrolysed by boiling alcoholic potassium hydroxide to the free lactamic acid, $\text{N} \cdot \text{CMe} = \text{C}(\text{CO}_2\text{H}) \cdot \text{C}(\text{CH}_3)_2 \text{NH}$, pale yellow, microscopic needles, decomp. 300°. Potassium hydrosulphide forms the thiolactone of ethyl hydrogen 2:6-dimethyl-4-thiolmethylpyridine-3:5-dicarboxylate, in long, silky, pale pink needles, m. p. 115—116°, and this may be hydrolysed to the free thiolactonic acid, decomp. 272°. Potassium cyanide produces ethyl 2:6-dimethyl-4-cyanomethylpyridine-3:5-dicarboxylate, in colourless needles, m. p. 66—67°.

Acetylacetoneamine and $\alpha\beta$ -dichloroethyl ether react in the presence of dilute aqueous ammonia to form 3:5-diacetyl-2:6-dimethyl-4-chloromethyl-1:4-dihydropyridine, pale yellow, hard needles, m. p. 151°, which may be oxidised by nitric acid to 3:5-diacetyl-2:6-dimethyl-4-chloromethylpyridine, colourless needles, m. p. 76—77°. This reacts with sodium iodide to form the corresponding iodo-derivative, m. p. 116—118°, and with alcoholic ammonia at 50—60° to give the "anhydride" of 3:5-diacetyl-2:6-dimethyl-4-aminomethylpyridine, $\text{N} \cdot \text{CMe} = \text{C}(\text{CMe}) \cdot \text{C}(\text{CH}_3)_2 \text{N}$, which crystallises in dark reddish-brown needles, decomp. above 136°.

Benzoylacetoneamine yields 3:5-dibenzoyl-2:6-dimethyl-4-chloromethyl-1:4-dihydropyridine, in sulphur-yellow needles, m. p. 183°, which forms a nitro-derivative, m. p. 168—169°, instead of suffering oxidation, when treated with nitric acid. J. C. W.

The Isatins which contain a Quinoleic Nucleus. J. MARTINET (*Compt. rend.*, 1918, 166, 998—1000).—Tetrahydroquinoline is converted by the action of ethyl mesoxalate into ethyl 1:7-trimethylenedioindole-3-carboxylate, m. p. 174° (compare A., 1913, i, 756). In the same way, the author has prepared ethyl 5-methyl-1:7-trimethylenedioindole-3-carboxylate, m. p. 162°, and ethyl 5-methyl-1:7- α -methyltrimethylenedioindole-3-carboxylate (annexed formula), m. p. 108°. These

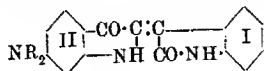


esters when hydrolysed by alkalis and the product acidified give the corresponding isatins, which yield salts of the intermediate, unstable isatoic acids. Thus 1:7-trimethyleneisatin, red needles, m. p. 195°, giving a phenylhydrazone, m. p. 150°, yields the potassium, copper, and lead salts of 1:7-trimethyleneisatoic acid; 5-methyl-1:7-trimethyleneisatin, m. p. 185°, gives a phenylhydrazone, m. p. 177°, and yields potassium and copper 5-methyl-1:7-trimethyleneisatoates; 5-methyl-1:7- α -methyltrimethyleneisatin, m. p. 165°,

gives a *phenylhydrazone*, m. p. 141°, and the *barium* salt of the corresponding isatoic acid. The isatins when treated with hydrocyanic acid and the cyano-compound hydrolysed with hydrogen chloride in alcoholic solution are reconverted into the dioxindole-3-carboxylic esters.

W. G.

Yellowish-brown Vat Dyes. SYNTHETIC PATENTS CO., NEW YORK (U.S. Pat. 1266092).—The new vat-dyes are compounds of the type

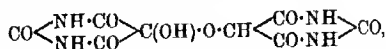


in which the benzene nucleus, I, contains halogen, the nucleus, II, may contain halogen, and R may be oxygen or hydrogen. As an example, the compound produced by the interaction of 5:7-dichloroisatin and 6-aminoindoxyl is cited; this is a dark brown, lustrous, crystalline powder, soluble in concentrated sulphuric acid with reddish-violet colour, which dyes cotton from the alkaline hypsulphite vat in yellowish-brown shades, fast to washing, light, and chlorine.

J. C. W.

Alloxan and Alloxantin. EINAR BILMANN and JOHANN BENTZON (*Ber.*, 1918, 51, 522–532).—Thunberg has recently shown that the solubility of alloxantin in water is greatly depressed by the addition of alloxan, and suggests, therefore, that alloxantin is the alloxan salt of dialuric acid (*A.*, 1916, i, 635). Some careful determinations of these solubilities have now been made, and the results show that the solubility of alloxantin in the presence of alloxan obeys the mass law, and that it is possible to calculate the dissociation constant for alloxantin.

According to Richter's oxonium formula (*A.*, 1911, i, 757), which is favoured by Thunberg, the dissociated particles would be an alloxan cation and a dialuric anion. Alloxan might be expected, therefore, to give the same cation in contact with hydrochloric acid, and consequently raise the freezing point of the acid, but in reality it has no such influence. Furthermore, solutions of alloxan become distinctly yellow on heating, but colourless again on cooling, owing to the formation and hydrolysis of the anhydride (*Biltz*, *A.*, 1913, i, 166). This shows that alloxan is very susceptible to hydroxyl compounds, and excludes a quinonoid configuration for both alloxan and alloxantin. In fact, the arguments advanced are in favour of the formula



for alloxantin. This "alcoholate" formula was first proposed by Slimmer and Stieglitz (*A.*, 1904, i, 634).

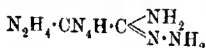
The solubility determinations were carried out in an atmosphere

of carbon dioxide or nitrogen, the apparatus being described. Alloxantin was determined by titration with a solution of iodine in potassium iodide, and alloxan + alloxantin found from the result of a Kjeldahl estimation. The solubility of alloxantin, $C_8H_6O_8N_4 \cdot 2H_2O$, in water at 25° is 0.2885 gram per 100 c.c. (or grams), of which about 22% is undissociated. The mean value of K at $25^\circ = 38.7$.

J. C. W.

The Action of Hydrazine Hydrate on Cyanotetrazole. I. LIFSCHITZ and W. F. DONATH (*Rec. trav. chim.*, 1918, **37**, 270—293).—A more detailed account of work already published (compare A., 1915, i, 465; 1916, i, 436), and an elaboration of the work of Curtius, Darapsky, and Müller (compare A., 1916, i, 84) in reply to these authors.

When the mixture obtained by passing cyanogen into aqueous azoimide is treated with hydrazine hydrate, in addition to the bishydrazonium salt of bistetrazole, there is obtained the hydrazonium salt of tetrazolecarbohydrazidine,



or $N_2H_4 \cdot CN_4H \cdot C \begin{smallmatrix} \text{NH} \\ \text{NH} \cdot \text{NH}_2 \end{smallmatrix}$, m. p. 276° , which gives a silver salt, and when treated with nitrous acid yields bistetrazole. The hydrazonium salt when treated with aldehydes gives condensation products having the general composition $CHR \cdot C_2H_3N_7$. Thus benzaldehyde gives a compound, m. p. 248° ; anisaldehyde a compound, m. p. 252° ; and *p*-nitrobenzaldehyde a compound, m. p. 240° .

The authors describe an ethyl derivative of ditetrazylidihydrotetrazine and an ethyl derivative of ditetrazyltetrazine. W. G.

Diazotisation of Nitrosobenzene. EUG. BAMBERGER (*Ber.*, 1918, **51**, 634—636).—Nitrosobenzene may be almost completely converted into a benzenediazonium salt by adding a very concentrated solution of sodium nitrite to a solution in cold acetic acid, or by means of amyl nitrite. The question is raised, which is the active agent, nitrous acid, nitrogen peroxide, or nitric oxide? No answer is given in the case of nitrous acid, but it has now been proved that dry nitrogen peroxide has no diazotising action, its only effect being that of an oxidising agent. Nitric oxide was shown some twenty years ago to convert nitrosobenzene into benzenediazonium nitrate.

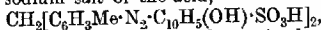
J. C. W.

Action of Di-*p*-diazotolylmethane Chloride on Naphthol- and Naphthylamine-sulphonic Acids. I. JAMES H. STEBBINS, jun. (*J. Ind. Eng. Chem.*, 1918, **10**, 445—448).—When *o*-toluidine is dissolved in dilute hydrochloric acid, mixed with formaldehyde, and kept at 70 — 76° for four hours, di-*p*-aminodi-*m*-tolylmethane, $C_6H_3(C_6H_4Me \cdot NH_2)_2$, is obtained; it crystallises in rhombic prisms, m. p. 149° . When this is diazotised, it yields di-*p*-diazotolyl-

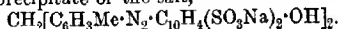
methane chloride, $\text{CH}_2(\text{C}_6\text{H}_3\text{Me}\cdot\text{N}_2\text{Cl})_2$. On mixing the diazotised solution with sodium α -naphthol-4-sulphonate, a copious, blood-red precipitate is obtained which seems to have the composition $\text{N}_2\text{Cl}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{SO}_3\text{H}$, and is gradually transformed into



The *sodium* and *barium* salts of the latter acid were prepared. In the presence of alcohol, two molecules of the naphtholsulphonic acid combine with the diazo-compound, and a heavy, carmine precipitate of the sodium salt of the acid,



is formed. The diazotised solution when mixed with an aqueous sodium carbonate solution of β -naphthol-3:6-disulphonic acid, yields a scarlet-red precipitate of the salt,



W. P. S.

Nucleic Acid and its Analytical Examination. A. CHASTON CHAPMAN (*Analyst*, 1918, 43, 259—263).—The chief difficulties in the preparation of pure nucleic acid are the complete removal of proteins and the prevention of the acid becoming contaminated with its own products of decomposition. Hydrolysis must therefore be effected under definite conditions. It is uncertain whether all nucleic acids are identical with one or other of the two typical nucleic acids obtained from yeast and from the thymus gland, but in practice yeast-nucleic acid is frequently described as "plant nucleic acid." Its chief products of hydrolysis are: guanine, adenine, cytosine, uracil, *d*-ribose (pentose), and phosphoric acid. Nucleic acid of animal origin, when hydrolysed, yields: guanine, adenine, cytosine, thymine, lactic acid (from a hexose), and phosphoric acid. Plant nucleic acid is a white, friable, odourless substance with the formula $\text{C}_{28}\text{H}_{50}\text{O}_{29}\text{N}_{15}\text{P}_4$. It is nearly insoluble in water, but is readily soluble in solutions of alkali acetates, from which hydrochloric acid precipitates it as a curd-like precipitate soluble in excess of the acid. It forms characteristic salts with copper, calcium, and silver, and a strong aqueous solution of sodium nucleate gelatinises. It may also be identified by yielding guanine and adenine as distinctive products of hydrolysis. [See, further, *J. Soc. Chem. Ind.*, 1918, 441A.] C. A. M.

The Nature of the Aqueous Medium in the Enzymic Hydrolysis of Oils. Y. TANAKA (*J. Chem. Ind., Tokyo*, 1918, 21, 112—117).—Referring to the experiments by Kita (A., 1918, i, 274), the author suggests that he was working with a lipase preparation still containing zymogen not completely activated by the previous treatment with acid, and consequently subject to a further stimulation when allowed to act on fats in an acidified medium. Further experiments have been made according to the author's method, by triturating pressed castor beans with eight

times their weight of *N*/10-acetic acid, washing, and drying the insoluble residue. A series of hydrolyses was carried out with 2 grams of the activated lipase powder and 25 grams each of soja bean oil at 38–39°, in 10 c.c. of aqueous substratum, containing increasing amounts of *N*/10-sulphuric acid. The percentage of oil hydrolysed in one hour decreased with increasing acidity of the medium, thus: with 0.0 c.c. acid, 58.4%; 0.5 c.c., 53.8%; 1.0 c.c., 51.2%; 2.0 c.c., 40.0%. The results after five hours were in the same order. Thus it is confirmed that castor bean lipase which has been treated with the optimum quantity of acid and washed acts most energetically in neutral media. J. F. B.

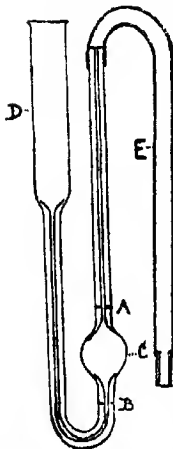
Action of Ethyl Alcohol and Acetone on Lipase. GEN-ITSU KITA and MINORU OSUMI (*J. Tokyo Chem. Soc.*, 1918, **39**, 13–22).—Connstein, Hoyer, and Wartenburg (*A.*, 1903, i, 218), Hoyer (*A.*, 1907, ii, 192), and Falk (*A.*, 1913, i, 664) have already observed that the activity of lipase is destroyed by ethyl alcohol. The author has repeated this investigation, and finds that when the activity of lipase has been destroyed by alcohol, it cannot be restored by any treatment. Contrary to the statements of Hoyer and Falk, acetone has no particular influence on the activity. S. F.

Physiological Chemistry.

Transport of Carbon Dioxide by Solutions of Sodium Hydrogen Carbonate. G. A. BUCKMASTER (*Proc. physiol. Soc.*, 1918, xvi—xvii; *J. Physiol.*, **52**; from *Physiol. Abstr.*, 1918, **3**, 177).—The dissociation tensions of solutions of varying quantities of pure sodium hydrogen carbonate in boiled-out water were determined at 38° in an atmosphere of air, nitrogen, and a mixture of nitrogen and carbon dioxide respectively. The average dissociation tension was 2.25 mm. of mercury in air and carbon dioxide respectively. In a mixture of nitrogen and carbon dioxide, with tensions of the latter within the range of alveolar air, there was no dissociation and carbon dioxide was actually absorbed, and it is therefore improbable that the transport of carbon dioxide in the blood is a function of the sodium carbonate. S. B. S.

Viscosity of Blood. J. W. TREVAN (*Biochem. J.*, 1918, **12**, 60–71).—The viscosimeter is blown from glass tubing of 0.8 mm. diameter for the large size, using 2 c.c. of blood, and 0.2 mm. diameter for the small form requiring only 1 c.c. of blood. In the large model, the bulb, *C* (see Fig.), holds rather less than 1 c.c.; the other dimensions are in proportion. The funnel, *D*, is made from a test-tube (1.25 cm.) drawn out and fused on, and holds about

5 c.c. The blood is mixed with a little hirudin in *D* and allowed to run into *C*. The instrument is then placed in a thermostat at 40° for ten minutes. The bulb, *C*, is then emptied into *D* by slowly blowing down the rubber tube, *E*, until the whole of the blood is in *D*. The corpuscles are mixed with the plasma by stirring with a coiled wire, and then the blood is allowed to flow back again into *C*, the time of flow from *B* to *A* being noted with a stop-watch, and the blood in *D* being stirred continually with the coiled wire.



The results show that the viscosity of the blood is directly proportional to that of the plasma over a very wide range of plasma viscosity provided the volume of corpuscles remains constant. Any increase in the number of corpuscles greatly increases the viscosity of the blood. The relation is expressed by the formula $100/P = (n/n - 1)^2$, where *P* is the percentage volume of corpuscles in the blood and *n* is the ratio of the viscosity of the whole blood to that of the plasma. The bearing of the results on the interpretation of certain phenomena associated with inflammation, infarction, and blood circulation generally are discussed.

H. W. B.

Physiology of Blood-sugar. II. Lépine's "Sucre virtuel."

RICHARD EGE (*Biochem. Zeitsch.*, 1918, 87, 92—103).—According to Lépine (numerous papers, 1902—1914), part of the sugar in blood is free ("sucre immedial"), whereas part is bound in chemical combination and only set free after hydrolysis ("sucre virtuel"). Using ferments and other treatment, the author has been unable to confirm Lépine's statement as to the existence of the two forms of blood-sugar.

S. B. S.

Influence of Morphine, and of Morphine with Ether Anæsthesia, on the Dextrose in the Blood. ELLISON L. ROSS (*J. Biol. Chem.*, 1918, 34, 335—342).—The subcutaneous injection of morphine into a dog is followed by a pronounced glycosuria, which, although not so intense as that which may be produced by simple ether anæsthesia, is nevertheless increased by subsequent administration of ether, so that the final degree of hyperglycæmia reached is approximately the same, either with or without the preliminary morphine injection.

H. W. B.

Rate of Dialysis of the Dextrose in the Blood in Experimental Diabetes. ISRAEL S. KLEINER (*J. Biol. Chem.*, 1918, 34, 471—487).—The rate of dialysis of dextrose from blood into Ringer's solution is dependent on the state of the animal from which the blood is obtained. The dextrose in the blood from a

diabetic animal dialyses at an irregular rate showing more or less completely arrested dialysis, usually about two hours after the commencement of the experiment. The dialysis of the dextrose in normal blood, to which dextrose has been added to bring it to the same dextrose content as the diabetic blood, occurs at a uniform rate. The author suggests that in diabetes the dextrose exists partly in a combined state in the blood, which tends to hinder its dialysis (compare Michaelis and Rona, A., 1909, ii, 68).

H. W. B.

Acetone Substances in the Blood in Diabetes. ERNEST LAURENCE KENNAWAY (*Biochem. J.*, 1918, 12, 120—130).—The concentration of acetone substances in the blood in diabetic coma may be equivalent, when reckoned as acetoacetic acid, to that of a 0.03*N*-solution; this amount is sufficient to combine with more than one-third of the sodium of the plasma.

H. W. B.

The Existence of Creatinine and Creatine in the Blood in Normal and Pathological Cases. III. Normal Cases, especially in Old Age. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, 87, 1—22).—The creatinine and creatine content in the blood of individuals of varying ages is tabulated according to the ages.

S. B. S.

The Presence of Phosphates in Human Blood-serum. VI. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, 87, 237—247).—A general summary of results dealing with the acid soluble and residual phosphorus in pathological cases, with the relationship between the lipid and residual phosphorus, and with leithinæmia in cases of mental diseases.

S. B. S.

Chemical Studies in Physiology and Pathology. IV. Hæmolysis. The Complement. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1918, 87, 36—76. Compare this vol., i, 241).—The authors develop further their conceptions as to the chemical and physical nature of proteins and the mode of action of proteoclastic ferments.

Hæmolysis, according to their views, depends on the destruction of the semipermeable structure of the membrane of the blood-corpuscles. This can be brought about either by mechanical or chemical means. Included in the former are such methods as the sudden transference of the corpuscles to hyper- or hypo-tonic solution, drying, etc. The chemical hæmolytics act either directly as solvents (especially for the lipid constituents) or they act as hydrolytic reagents on lipoids or proteins, or on both.

The agglutination of erythrocytes follows the same laws as that of bacteria and other "hydrophil" suspensions, and is connected intimately with the hydrophil capacity of the surfaces.

In the action of the complement, two functions are to be distinguished. (1) That of the "middle-piece," which is a globulin precipitation and renders the surface of the blood cells more capable

of taking up certain degradation products of the serum ("persensitisation") which form the constituents of the "end-piece."
 (2) The "end-piece" function consists in the direct solvent or hydrolytic action of the degradation products contained in the albumin fraction. The chief influences which inhibit or destroy the complement action can be ascribed to actions on the globulins, which render these substances too stable and less liable to be precipitated, such as dilution with water, Brand's modification, addition of citrates, oxalates, acids, alkalis, action of heat, etc. Other "anti-complement" actions consist in removal of the globulins from the serum, such as addition of precipitants of globulins, bacteria, agar, and cobra-poison. S. B. S.

Action of Symbiotic Bacteria on the Constituents of Fats. HENRI BIERRY and PAUL PORTIER (*Compt. rend.*, 1918, 166, 1055—1057).—The symbiotic bacteria isolated from the testicle of a pigeon oxidise glycerol in a yeast bouillon, giving a C_8 sugar, glycerose, but the same organisms in a chemically definite medium containing asparagine, glycerol, nitrate, etc., give no trace of dihydroxyacetone. The symbiotes also cause β -oxidation, acet-aldehyde and acetone being obtained from β -hydroxybutyric acid and from butyric acid. W. G.

Importance of the Ketonic Function in Metabolism. Its Creation by Symbiotic Bacteria. PAUL PORTIER and HENRI BIERRY (*Compt. rend.*, 1918, 167, 94—96. Compare preceding abstract).—It is shown that the symbiotes of mammals and birds are capable, in suitable medium, of converting pentoses, hexoses, disaccharides, and certain polyhydric alcohols into acetylmethylcarbinol, amongst other products. On the other hand, when the conditions of the medium are suitable, they are capable of synthesising polysaccharides, the yield of the latter being greatest when a ketose is present. It is also noted that the production of a polysaccharide by symbiotic action is always accompanied by the production of alkalinity in the medium. W. G.

Sugar Metabolism and Diabetes. H. McGUIGAN (*J. Lab. and Clin. Med.*, 1918, 3, 319—337; from *Physiol. Abstr.*, 1918, 3, 182—183).—Attention is directed to the variations found in the reducing substances in the blood caused by differences in the concentration of the alkali, and of salts when the latter have been used for precipitating the proteins. There is apparently no difference in the condition of sugar in the blood in normal and in diabetic cases. Observations on utilisation of sugar in muscular contraction, on effect of vascular changes in the liver on glycogenolysis, and on peptone hypoglycæmia are recorded. S. B. S.

The Water-soluble Accessory Growth-promoting Substance. II. Its Influence on the Nutrition and Nitrogen Metabolism of the Rat. JACK CECIL DRUMMOND (*Biochem. J.*, 1918, 12, 25—41).—When rats are fed on an artificial diet deficient

in the water-soluble accessory substance, the only apparent deviation from the normal nitrogen metabolism is the appearance of creatinuria, accompanied by a slow wasting of the skeletal muscles. The food consumption is low; it may be increased by the addition of flavouring agents, such as meat extract, to the diet, but unless this agent contains the water-soluble accessory, growth does not occur. The addition to the inadequate diet of extracts containing the water-soluble substance causes a greatly increased intake of food, immediately followed by growth. The amount of growth is, within certain limits, proportional to the amount of accessory substance added, provided that the diet is adequate in other respects. The length of time that a rat is able to maintain itself on a diet deficient in the water-soluble substance without suffering a serious loss of body-weight is directly proportional to the age at which the restriction is imposed. Actively growing animal tissues (embryos, tumours) do not contain appreciable amounts of the water-soluble accessory substance; desiccated pituitary, thyroid, and thymus glands, and testicular and ovarian tissues, are also deficient in this respect.

H. W. B.

The Utilisation of Yeast in the Animal Organism.

EMERICH SCHILL (*Biochem. Zeitsch.*, 1918, 87, 163—175).—Experiments on dogs indicated that the proteins of yeast can not only be resorbed by the organism, but can produce a positive nitrogen balance. About half the chemical energy of yeast can be utilised by the organism.

S. B. S.

Influence of the Species of Animal on the Toxicity and Mode of Utilisation of Alimentary Proteins.

E. MAIGNON (*Compt. rend.*, 1918, 167, 91—94).—Feeding experiments, similar to those carried out with white rats, have been performed with dogs, the same three proteins (egg-albumin, fibrin, casein) being used. The dog accommodates itself much better than the rat to a purely protein diet, and was able to retain its weight for a considerable time on casein or meat powder alone. On the other hand, casein is much more toxic for dogs than for rats. Whereas rats on this diet died from exhaustion of their reserves, dogs died undoubtedly as a result of toxic action. The toxicity of a given protein varies from one species of animal to another apparently inversely as the ease with which the animal can transform the protein into fat.

W. G.

Digestion of the Proteins of Cooked Meat in Dogs with Ligatured Carotid Arteries.

ENGARN ZUNZ (*Biochem. J.*, 1918, 12, 42—59).—After the ligature of the carotids, a meat meal is retained in the stomach for a longer time than occurs in the normal animal, due, apparently, to an altered blood supply to, or innervation of, the stomach produced by the operation.

H. W. B.

Origin of the Conception of Physiologically Balanced Salt Solutions.

JACQUES LOEB (*J. Biol. Chem.*, 1918, 34, 503—504).—The author claims to have originated the conception

of physiologically balanced salt solutions (*Amer. J. Physiol.*, 1899—1900, **3**, 445).
H. W. B.

Active Substances in Glands with Internal Secretions. ERNST BERLIN (*Zeitsch. Biol.*, 1918, **68**, 371—390).—Extracts of spleen contain, besides choline, a substance which exerts a powerful action on the muscles of the uterus and intestine. The latter substance is not β -amino-4-ethylglyoxaline. Both choline and the unknown substance occur also in a commercial extract of spleen called hormonal.
H. W. B.

The Genesis of Thiocyanic Acid in Animals. S. DEZANI (*Arch. farm. sper. sci. aff.*, 1917, **24**, 113—128; from *Physiol. Abstr.*, 1918, **3**, 164).—Thioacetamide does not give rise to thiocyanic acid in the dog, and thus the hypothesis of Röhmann as to its genesis from fatty nitriles through the corresponding thioamides or thioamidic acids is not substantiated. In the dog, the ingested nitrile is partly transformed into thiocyanic acid and partly eliminated as such. The remainder is transformed into products which have not yet been identified.
S. B. S.

Anti-scorbutic Value of Cow's Milk. HARRIETTE CHICK, ELEANOR MARGARET HUME, and RUTH FILBY SKELTON (*Biochem. J.*, 1918, **12**, 131—153).—Guinea-pigs grow when fed on a diet of oats and bran with milk which has been heated at 120° under pressure, but they rapidly develop scurvy. If some fresh, unheated milk is added to the diet, scurvy may appear sooner or later, according to the amount of milk in the daily ration. By greatly increasing the amount of milk so that the daily ration exceeds 100 c.c., the onset of scurvy is entirely prevented. Milk is therefore relatively poor in the anti-scorbutic accessory substance, and it is most essential that, for the prevention of scurvy, infants fed on milk which has been previously heated or dried should also be given orange juice, raw swede juice, or similar material rich in the anti-scorbutic vitamine. A connexion between scurvy and chronic constipation (McCollum and Pitz, A., 1917, i, 604) is not confirmed.
H. W. B.

Milk as a Source of Water-soluble Vitamine. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1918, **34**, 537—551).—The authors find that vigorous growth of rats does not occur on diets in which the water-soluble vitamine is supplied by milk unless considerable quantities of the milk are consumed. Milk does not contain, therefore, as much water-soluble vitamine as Hopkins's experiments (A., 1912, ii, 779) would lead one to expect (compare preceding abstract).
H. W. B.

Carbon Dioxide Content of Urine. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1918, **34**, 569—575).—The total amount

of free and combined carbon dioxide passed in the urine in twenty-four hours by a normal person may vary from 4 to 400 c.c., according to the nature of the ingested food. Vegetable food increases and animal food decreases the output of carbon dioxide in the urine. The carbon dioxide present in the urine varies inversely, although not proportionately, with the hydrogen ion concentration.

H. W. B.

Creatine and Creatinine. VIII. Alleged Exogenous Origin of Urinary Creatine in the Protein of the Diet.

WILLIAM C. ROSE, J. STERLING DIMMITT, and H. LEIGH BARTLETT (*J. Biol. Chem.*, 1918, **34**, 601—612).—The authors find that the ingestion of diets excessively high in protein fails to induce the excretion of creatine in normal men and women. The theory that creatine has an exogenous origin in the protein of the diet is not confirmed (compare Denis, Kramer, and Minot, A., 1917, i, 526).

H. W. B.

Examination of the Faeces of Rabbits Fed on a Diet of Cabbage for the Occurrence of a Phytosterol. The Phytosterols in Cabbage Seeds and Grass Fruits. MARY TAYLOR ELLIS (*Biochem. J.*, 1918, **12**, 154—159).—The faeces of rabbits fed on cabbage do not contain a typical phytosterol, but a trace of a substance resembling coprosterol, melting at 102°, may be detected. Cabbage seeds contain a relatively large amount of phytosterols similar to those present in rape oil. Grass fruits contain a trace of phytosterol, together with chortosterol (compare Dorée and Gardner, A., 1908, ii, 514).

H. W. B.

Biochemistry and Chemotherapy of Tuberculosis. XVI.

Pharmacology and Toxicology of Copper Salts of Amino-acids. HARRY L. HUBER (*J. Pharm. Exp. Ther.*, 1918, **11**, 303—329).—The copper salts of leucine, glycine, and glutamic acid produce exactly the same physiological effects as copper sulphate when administered in various ways to guinea-pigs and rabbits.

H. W. B.

Effect of Intravenous Injections of some Sodium Salts with Special Reference to the supposed Toxicity of Sodium Phosphate. ISIDOR GREENWALD (*J. Pharm. Exp. Ther.*, 1918, **11**, 281—301).—The intravenous injection of neutral solutions of sodium chloride, sulphate, and phosphate into dogs produces changes in the volume, osmotic pressure, and reaction of the blood, and results in disturbances of the normal relations between the various ions of the blood and tissues. It is to these physical factors rather than to a direct toxic action of the phosphate ion that the ill-effects observed after the administration of sodium phosphate solutions are to be ascribed (compare Binger, A., 1917, i, 677). Muscle twitching, tetany, and violent convulsions may be produced by the injection of the chloride and sulphate, as well as of the

phosphate of sodium, and seem to be dependent more on the sodium than on the phosphate ion, since a balanced solution containing high concentrations of sodium, potassium, and calcium in certain fixed proportions may be introduced without producing any ill-effects. The injection of sodium salts is followed by the elimination of both potassium and calcium salts in the urine, but whereas the content of calcium in the blood and serum falls, that of potassium remains unchanged. Similarly, the injection of either sodium sulphate or phosphate, as well as of the chloride, occasions an increased elimination of chlorides in the urine, probably due to differences in the permeability of the kidneys to the different salts. H. W. R.

Metabolism of the Mustard Oils. W. H. PETERSON (*J. Biol. Chem.*, 1918, **34**, 583—600).—The addition of allylthiocarbimide, 0.2 to 0.4 gram per day, and allyl sulphide, 0.5 to 1 gram per day, to the starchy diet of a pig produces a gradual rise in the total sulphur excreted in the urine, which persists for ten to twelve days after the ingestion of these compounds has ceased. This points to a very slow metabolism and the inability of the body to dispose readily of them. These compounds are not oxidised during their passage through the body, but are converted into a non-volatile, less toxic substance which has not been identified. From 40 to 70% of the sulphur in the ingested compound can be subsequently recovered from the urine, the remainder being probably eliminated in the form of volatile compounds through the lungs and skin. The two sulphur compounds are practically completely absorbed, scarcely a trace being excreted in the faeces.

H. W. B.

The Behaviour of Urotropine and Formaldehyde in the Organism. E. SALKOWSKI (*Biochem. Zeitsch.*, 1918, **87**, 143—162).—The author has investigated the various reactions for formaldehyde with the object of detecting this substance in the presence of much larger quantities of urotropine. The only quite satisfactory reaction for this purpose was found to be that of Jorissen as modified by Vanino (with phloroglucinol and sodium hydroxide. *A.*, 1899, ii, 703). Solutions of urotropine cannot be kept without decomposition for any great length of time; they are somewhat more stable in the presence of sodium carbonate (0.1—1%), and such solutions can be kept without appreciable change for a week. In the presence of slight amounts of acid, solutions alter from day to day. There is, apparently, a scission of formaldehyde from urotropine, which takes place in the stomach. Examination of the urine after ingestion of urotropine reveals the fact that it is partly excreted unchanged, and partly oxidised to formic acid.

S. B. S.

Atophan and some of its Derivatives. LUISE ROTTEN (*Zeitsch. exp. Path. Ther.*, 1917, **19**, 176—197; from *Physiol. Abstr.*, 1918, **3**, 194—195).—Atophan (2-phenylcinchonic acid) is

toxic to cold-blooded, but not to warm-blooded animals. It paralyzes both the central nervous system and the nerves of the heart of frogs, and the heart generally stops beating in systole. Atophan owes its activity to the linking up of a phenyl group to a quinoline nucleus, as quinolinecarboxylic acid is almost inactive. Other substitution products were investigated, and generalisations as to chemical constitution and pharmacological action are made. No substance antagonistic in action to atophan was discovered. After ingestion by the mouth in man, hydroxyphenylquinolinecarboxylic acid is excreted in the urine, together with an increased amount of uric acid. To the former the increased output of uric acid is ascribed, as such an increased excretion can be produced by its direct administration.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Action of Cyanohydrins on Ferments and Bacteria.

MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **87**, 129—134).—The action of the urease of soya bean is strengthened by the presence of the cyanohydrin of acetaldehyde, but inhibited by the corresponding propaldehyde derivative. Both compounds inhibit strongly the ferment formation by bacteria, whilst they exert only a very moderate deleterious action on the bacteria themselves.

S. B. S.

The Degradation of Tyrosine by *Bacterium coli phenologenes*, and the Composition of Human Urines containing Phenol.

M. RHEIN (*Biochem. Zeitsch.*, 1918, **87**, 123—128).—Phenol is formed by *Bacterium coli phenologenes* only from tyrosine and *p*-hydroxybenzoic acid. It was not formed from the following (possible intermediary degradation products of tyrosine): *p*-hydroxyphenylpropionic acid, *p*-hydroxyphenylacetic acid, *p*-hydroxyphenylpyruvic acid, *p*-hydroxyphenylethylamine, *p*-hydroxyphenylethyl alcohol, *p*-hydroxyphenyl- α -lactic acid, and *p*-cresol. It appears, therefore, that tyrosine is degraded by attack of the 8-carbon atom of the alanine chain and simultaneous oxidation. Phenol and *p*-cresol in human urines can be detected readily by the colour reactions with formaldehyde-sulphuric acid and with diazobenzenesulphonic acid in sodium carbonate solutions.

S. B. S.

The Influence of Lactic Acid on Lactic Acid Fermentation.

W. VAN DAM (*Biochem. Zeitsch.*, 1918, **87**, 107—122).—Investigations were made to ascertain whether the stoppage of fermentation by the coccid form of bacteria is due to the action of the hydnion

of the lactic acid produced or to the undissociated molecule. The conclusion is drawn that the stoppage is due to both. If sodium lactate is added to the whey, further acid formation ceases when the concentration of the undissociated molecule reaches 0.01*N*. In such cases, the final hydron concentration fails to reach the toxic amount of about 10×10^{-5} . If hydrochloric acid is added to the whey before inoculation, so much lactic acid is formed as to bring the final hydron concentration to $10\text{--}20 \times 10^{-5}$ *N*. In this case, the amount of undissociated lactate remains below the toxic amount. Attention is directed to the fact that certain conclusions of other authors as to the value of the nitrogenous nutrients are vitiated by their failing to take into account their buffer action.

S. B. S.

The Bacterial Degradation of *d*-Tyrosine, with Special Reference to the Stereochemical Configuration of the Degradation Products. M. TSUBOI (*Acta. Schol. Med. Kyoto*, 1918, **2**, 115—123; from *Physiol. Abstr.*, 1918, **3**, 165).—A continuation of previous work (A., 1917, i, 679). Although in degradation of the *dl*-form, the *l*-form is rapidly acted on, the *d*-form does not remain entirely intact, and can be slowly broken down by *Bacterium subtilis* or *B. proteus* in media containing phosphates. The same products are obtained whether *dl*-, *d*-, or *l*-tyrosine is used as substrate, namely, *d*-*p*-hydroxyphenyllactic acid by the action of *B. proteus* and the corresponding *l*-acid by the action of *B. subtilis*. It is suggested that in both cases the inactive *p*-hydroxyphenylpyruvic acid is formed as an intermediate product.

S. B. S.

By-products of the Fermentation of Cabbage. V. E. NELSON and A. J. BECK (*J. Amer. Chem. Soc.*, 1918, **40**, 1001—1005).—The fermented cabbage examined was the ordinary commercial material, "sauerkraut." The volatile acidity represented from 25–50% of the total acidity. The volatile acids consisted of acetic and propionic acids, no higher acids being present, although in two cases formic acid was isolated. The fixed acidity was in all probability due to an inactive form of lactic acid. Alcohols were present to the same extent as volatile acids, and consisted entirely of ethyl and propyl alcohols. Esters, present only in small amount, contributed an essential part in the flavour and aroma. Mannitol was present in the fermented cabbage to the extent of 2.0–2.5%, and must have arisen from bacterial decomposition of the carbohydrates, since none is present in the natural plant.

W. G.

Formation of Esters of Phosphoric Acid during Alcoholic Fermentation. ALEXANDRE LEBEDEV (*Biochem. J.*, 1918, **12**, 87–92).—By treatment of a fermenting solution containing yeast, sucrose, and phosphates with alcohol, a mixture of esters of phosphoric acid can be isolated which yields an osazone, $C_{33}H_{51}O_7N_3P$;

this appears to be the osazone of an ester of phosphoric acid containing one molecule of the latter combined with a molecule of hexose and a molecule of triose. The osazone or mixture of osazones melts at 142—144°; a *p*-bromophenylosazone, m. p. 141—142°, and a barium salt have also been isolated, and in each case have been found to possess different properties from those associated with the corresponding compounds of ordinary hexose phosphate.

H. W. B.

Fermentation of Glyoxylic Acid. ALEXANDRE LEBEDEV (*Biochem. J.*, 1918, 12, 81—86).—Dried yeast (Lebedev) decomposes glyoxylic acid, forming carbon dioxide and acetaldehyde.

H. W. B.

Nature of the Proteolytic Enzyme of Yeast. NICOLAUS (VANOV (*Biochem. J.*, 1918, 12, 106—119).—When autolysing yeast is treated with potassium hydrogen phosphate, the decomposition of protein is accelerated, resulting in an increased production of peptones. A similar accumulation of peptones occurs when the autolysis proceeds at a relatively high temperature (54°). If, however, the autolysis proceeds in an alkaline medium, the decomposition of the proteins is inhibited, whilst a large production of amino-acids is obtained. Apparently the proteolytic enzyme of yeast is composed of two factors, a protease acting on proteins and forming peptones, and a peptase transforming the peptones into amino-acids. By varying the conditions in the manner indicated above, it is possible to inhibit the action of one factor without interfering with the activity of the other. It is probable that the peptase of yeast is identical with animal erepsin.

H. W. B.

Differential Behaviour of the Antineuritic and Antiscorbutic Factors towards Adsorbents. ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1918, 12, 93—105).—The anti-neuritic substance present in autolysed yeast is quantitatively adsorbed by fuller's earth or by dialysed iron. When a mixture of equal volumes of autolysed yeast (containing the anti-neuritic factor) and orange juice (containing the anti-scorbutic factor) is treated with fuller's earth, the anti-neuritic factor is entirely removed, whilst the anti-scorbutic activity remains unaltered. So far, it has not been found possible to separate the anti-neuritic substance in an active form from the fuller's earth adsorption complex.

H. W. B.

The Formation of Nitrites from Nitrates in Aqueous Solution by the Action of Sunlight and the Assimilation of the Nitrites by Green Leaves in Sunlight. BENJAMIN MOORE (*Proc. Roy. Soc.*, 1918, [B], 90, 153—167).—Dilute solutions of nitrates exposed either to sunlight or to a light-source rich in light energy undergo conversion into nitrites. If leaves are immersed in the nitrate solutions, comparatively little nitrite accumulates.

Nitrates taken up by plants from soil would, in the presence of sunlight, be converted into nitrites, which are more reactive, and it is held by the author that the early stages of synthesis of nitrogenous compounds are carried out by the green leaf, aided by sunlight. Rain-water collected for a considerable time contains no nitrites, all having been oxidised to nitrates, but if exposed to light for a few hours, a strong reaction for nitrites is obtained. Freshly-collected rain-water or dew contains both nitrates and nitrites. Air bubbled through nitrite- and nitrate-free water gives a reaction, when the water is tested afterwards for nitrates and nitrites showing the presence of both forms of oxides of nitrogen in air. The "ozone" odour in air is probably due to oxides of nitrogen formed by the action of sunlight rich in ultra-violet light in the upper layers of the atmosphere on air and water-vapour. S. B. S.

The Carbohydrate Nutrition of Plants. T. BOKORNY (*Biol. Zentr.*, 1916, **36**, 385—403; from *Physiol. Abstr.*, 1918, **3**, 208).—De-starched *Spirogyra* in water free from carbon dioxide can form starch in light from lactose, galactose, raffinose, dextrose, methyl alcohol, glycerol, ethyl acetate in the presence of monohydrogen dipotassium phosphate, and formaldehyde. It does not form starch under similar conditions from lavallose, sorbose, arabinose, xylose, rhamnose, acetone, and a number of other organic substances. Yeasts can apparently use methyl alcohol as a source of carbon only in the presence of dextrose or sucrose. S. B. S.

Metachromatin and the Phenolic Compounds of the Plant Cell. A. GUILLERMOND (*Compt. rend.*, 1918, **166**, 958—960).—The substance existing in the higher plants described by Dangeard as metachromatin is not comparable with the metachromatin of fungi. It is a phenolic compound capable of being converted into anthocyanin, which is formed thus by a chemical transformation of this compound, and not by fixation on it. The presence of this compound in the vacuole is not general, only being localised in special tissues. W. G.

The Constitution of a Plant Salt coming from the Cameroons. A. LACROIX (*Compt. rend.*, 1918, **166**, 1013—1015). Compare Dybowski and Demoussy, *ibid.*, 1893, **116**, 398).—The salt is obtained by lixiviation of the plant ashes of a grass, which is probably *Panicum crus Galli*, L. Its principal ingredients are: Cl=42.81%; SO_3 , 5.24%; K_2O , 56.73%; Na_2O , 1.63%; CaO , 1.19%, and a little magnesia, silica, and organic matter. Mineralogically, it is found to contain sylvine, sodium chloride, magnesium chloride, syngenite, and glaserite. W. G.

Transformation of Inulin by Autohydrolysis in the Tubercles of Asphodels. E. COUVREUR (*Compt. rend. soc. biol.*, 1918, **81**, 40—41; from *Physiol. Abstr.*, 1918, **3**, 201).—Inulin differs from inulin in its mode of crystallisation in fine needles. Maltose is not present in the tubercles of the fresh tissues of

Asphodel crasiferus and *A. microcarpus*, but appears after they have been triturated with water, and can be identified by the osazone test.

S. B. S.

Chemistry of the Cotton Plant, with Special Reference to Upland Cotton. ARNO VIEHOEVER, LEWIS H. CHERNOFF, and CARL O. JOHNS (*J. Agric. Research*, 1918, 13, 345—352. Compare Perkin, T., 1909, 95, 1855, 2181; 1916, 109, 145).—Quercimeritrin and isoquercitrin, previously isolated by Perkin (*loc. cit.*) from other types of cotton plant, have now been found in Upland cotton (*Gossypium hirsutum*). The leaves and flowers, with petals removed, contain quercimeritrin, whilst the petals contain this and isoquercitrin. Gossypitrin and gossypetin, which have been isolated from other types of cotton, could not be found in Upland cotton. The authors also isolated an ethereal oil from *G. hirsutum* differing from that found by Power and Browning (compare A., 1914, i, 1163) in the root bark of *G. herbaceum*. The new oil, present only to the extent of 0.0015 to 0.0071%, distils mainly between 200° and 300°, and leaves a black, empyreumatic residue; it is attractive to the boll weevil.

W. G.

Chemistry and Histology of the Glands of the Cotton Plant, with Notes on the Occurrence of Similar Glands in Related Plants. ERNEST E. STANFORD and ARNO VIEHOEVER (*J. Agric. Research*, 1918, 13, 419—436).—For the most part botanical. The glands in portions of the plant which are exposed to light are surrounded by an anthocyanin-bearing envelope of flattened cells, and contain quercetin, probably partly or wholly in the form of its glucosides, quercimeritrin or isoquercitrin, ethereal oils, resins, and perhaps tannins. The glands not normally exposed to light contain gossypol, and are surrounded by cells not containing anthocyanins. Gossypol is formed in the glands of the developing corolla, and on their exposure to light it is replaced by quercimeritrin. In the unfolding cotyledons, gossypol is changed, probably through oxidation, without the formation of quercimeritrin.

W. G.

The Active Glucosides of Digitalis Leaves of Various Origin and some Commercial Galenicals Compared Quantitatively. ERNST MEYER (*Arch. exp. Path. Pharm.*, 1917, 81, 261—288).—Kraft's gitalin (A., 1911, i, 734; 1912, i, 373) is very readily soluble in chloroform, but not in water; yet it cannot be extracted by chloroform from perfectly dry leaves, or from a cold water leaf-extract which has been completely dried over sulphuric acid. The addition of very little water to the dried extract, however, again renders the gitalin soluble in chloroform, and hence it can also be extracted from fresh leaves by chloroform. The extraction of gitalin from the leaves by cold water is attributed to the presence of tannins (see following abstract), from which the gitalin may be separated by chloroform.

Of commercial preparations, digalen and its copy digipan contain gitalin, and are probably cold water extracts. Digipuratum and digitalysatum contain only a portion of the gitalin and correspond with hot water infusions. G. B.

The Amount of Substances with a Digitalis Action in Oleander Leaves and the manner of their Natural Occurrence (Tannoid Question). WALTHER STRAUB (*Arch. exp. Path. Pharm.*, 1918, **82**, 327—343).—The activity of oleander leaves is about 2.5 times as great as that of digitalis leaves. Two crystalline active glucosides have been obtained by Böhringer & Söhne. One of these, *oleandrin* (C 67.85%, H 7.74%), is very active, about as much so as amorphous *k*-strophantiu, and is almost insoluble in water when pure. Amorphous active glucosides are also present in larger amount. Nevertheless, the whole of the active substances are readily extracted by cold water, and this solubility seems due to the large amount of a phenolic glucoside present in the leaves, which is not a true tannin. This substance is coloured green by ferric chloride, and is also present in digitalis leaves, but in smaller amount, so that the whole of the active substances of digitalis are not extracted by cold water. (See preceding abstract.) G. B.

Action of Normal Salts on Humus and other Experiments on Soil Acidity. LOUIS J. GILLESPIE and LOUIS E. WISE (*J. Amer. Chem. Soc.*, 1918, **40**, 796—812. Compare Gillespie, A., 1916, i, 303; Sharp and Hoagland, *J. Agric. Research*, 1916, **7**, 123).—The addition of solutions of chloride of sodium, potassium, or barium to humus causes a large increase in the hydrogen ion concentration as measured electrometrically, but as similar although smaller effects are observable in the action of potassium chloride on true solutions in the absence of humus or of undissolved solid matter, great care is required in drawing conclusions as to the mechanism of the process in the case of humus. At equivalent concentrations, barium chloride exerted the greatest influence on the electrometric potential of humus preparations. Considerable precaution is necessary in using litmus for the detection of acidity of soils, because even in very dilute solutions of hydrochloric acid the result is largely influenced by the "buffer" action of the solution under test. It is improbable that soils can act on litmus solely by virtue of their adsorptive power, and the difference in the effect of a moistened soil and of its aqueous extract on litmus may be due to the sparing solubility of the acidic organic substances of the soil. It is inadvisable at present to attempt broad general explanations of the cause of soil acidity, but the investigations with the hydrogen electrode and suitable indicators supply ample evidence of the common occurrence and wide distribution of truly acid soils in the United States. D. F. T.

General and Physical Chemistry.

Optics of Disperse Systems. II. I. LIFSCHITZ and JENS BRANDT (*Kolloid Zeitsch.*, 1918, **22**, 133—143. Compare this vol., ii, 181).—The refractive power of disperse systems has been examined by observations on colloidal solutions of sulphur and on soap solutions.

The results obtained with colloidal solutions of sulphur, fractionated by the method described by Odén, show that the refractive index increases with the concentration of the solution (grams per 100 c.c.) according to a linear equation. The density of the sols also increases with the concentration in an approximately linear manner. The value of $(d_s - d_0)/c$, in which d_s is the density of a sol of concentration c and d_0 the density of the solvent, is, however, much greater than for solutions of sulphur in carbon disulphide in which the sulphur is present in the molecular condition. The refractivity, measured by Gladstone and Dale's formula, is much more nearly constant than it is when the formula of Lorenz and Lorentz is employed.

The results obtained in measurements of the refractive index of aqueous solutions of sodium oleate, palmitate and stearate, and of potassium palmitate at 70° show that the refractive index changes with the concentration according to a linear formula. The molecular refractivities of the soaps appear to be independent of the concentration, and consequently of the degree of dispersity and of the extent to which the soaps are hydrolysed and dissociated.

H. M. D.

Effect of an Electric Field on the Spectrum Lines of Helium. TOSHIO TAKAMINE and USABURO YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 325—334).—The mode of resolution of the lines $\lambda 5048$, $\lambda 5016$, $\lambda 4922$, $\lambda 4472$, $\lambda 4438$, $\lambda 4388$, and $\lambda 4121$ under the influence of electric fields varying in intensity between 3000 and 70,000 volts per cm. is described. With the exception of $\lambda 4686$, the resolution of all the helium lines examined has been found to be unsymmetrical with respect to the initial line.

H. M. D.

Effect of an Electric Field on the Spectrum Lines of Hydrogen. II. TOSHIO TAKAMINE and USABURO YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 321—323. Compare A., 1917, ii, 402).—The changes produced by the action of a strong electric field have been examined by the investigation of a further series of hydrogen lines. The photographs show that the outer components of the lines belonging to the Balmer series frequently extend into the region of the unaffected secondary lines. The apparent lack

of any connexion between the two groups of lines suggests that they are due to different carriers. H. M. D.

Effect of an Electric Field on the Spectrum Lines of Hydrogen. SHIGEHARU NITTA (*Mem. Coll. Sci. Kyoto*, 1917, 2, 349—355. Compare preceding abstract).—The Stark effect has been examined with electric fields of considerably greater intensity than those used by previous observers. The H_{β} line yields six components, the separation of which is proportional to the intensity of the field. In addition to the Balmer lines, certain lines belonging to the secondary spectrum were investigated. H. M. D.

Optical Investigations on the Constitution of the Nitrates. KONR. SCHAEFER (*Zeitsch. wiss. Photochem.*, 1918, 17, 193—217. Compare A., 1910, ii, 562; 1917, ii, 61, 186).—The ultra-violet absorption of aqueous solutions of various nitrates has been examined over a considerable range of concentration. The results obtained for glucinum, silver, thallous, copper, mercurous, cerous, bismuth, and thorium nitrate are shown in the form of logarithmic absorption curves. On examining the available data for the nitrates, it would seem that these may be divided into three groups according to their optical behaviour at different concentrations. The nitrates of the alkali and alkaline earth metals satisfy the requirements of Beer's law. This relation is only approximately satisfied by the nitrates of glucinum, magnesium, aluminium, manganese, zinc, cadmium, lead, cobalt, and nickel, which form the second group. The deviations are partly due to hydrolysis and in part to the superposed absorption effect of the metal. To the third group belong the nitrates of metals which show large divergences from Beer's law. The absorption of the nitrates in this group (copper, silver, thallous, mercurous) increases rapidly with increase in the concentration of the solutions. This grouping of the metallic nitrates shows an undoubted connexion between the optical properties and the electro-affinity of the metals. The nitrates of the strongly electropositive metals show the selective absorption which has been attributed to that arrangement of the atoms which is found in the nitrate ion, as distinguished from the non-selective absorption of the grouping which is characteristic of the organic nitrates and of concentrated nitric acid. The absorption exhibited by the nitrates of the weak electropositive metals cannot be satisfactorily explained in terms of these two forms of the nitrate group, and it is suggested that the optical behaviour affords evidence of a third configuration of the atoms in the nitrate group.

The absorption of fused potassium nitrate has also been examined, and the selective absorption which it exhibits resembles closely that found for aqueous solutions of the alkali nitrates. In this respect it differs markedly from the absorption of anhydrous nitric acid, which shows no selective effect, although this is shown by dilute aqueous solutions of the acid. H. M. D.

Spectral Reaction of Methylfurfuraldehyde and β -Hydroxy- δ -methylfurfuraldehyde. (KINTARŌ OSHIMA and TETSUTARŌ TADOKORO (*J. Tokyo Chem. Soc.*, 1918, **39**, 23—30. Compare Oshima and Tollens, A., 1901, ii, 484).—A comparison of the absorption spectrum of samples of hydroxymethylfurfuraldehyde (as phloroglucide in hydrochloric acid solution) from various sources shows identity of the substance prepared by Kiermayer's method with that obtained from dextrose, levulose, or inulin by distillation with hydrochloric acid. With hydroxymethylfurfuraldehyde prepared from galactose and lactose, the absorption band is shifted a little towards the F-line, and even slightly overlaps that line in the case of samples prepared from sucrose. These different absorption spectra can, however, be readily distinguished from that given by methylfurfuraldehyde. S. H.

The Relationship between the Optical Rotatory Powers and the Relative Configurations of Optically Active Compounds. The Influence of certain Inorganic Haloids on the Optical Rotatory Powers of α -Hydroxy-acids, α -Amino-acids, and their Derivatives. GEORGE WILLIAM CLOUGH (T., 1918, **113**, 526—554).—The author has compared the effect of sodium haloid salts on the optical rotatory powers of *l*-lactic, *d*-glyceric, *l*-malic, and *d*-tartaric acids and certain of their esters, and the effect of introducing a given radicle into the molecules of the configuratively similar hydroxy-acids, *l*-lactic, *l*-glyceric, *d*-malic, and *d*-tartaric acids, and from his results assumes that the optical rotatory powers of similarly constituted compounds possessing the same configuration are in general influenced similarly by the same changes in the external conditions and also by the introduction of the same substituent into a given radicle attached to the asymmetric carbon atom. The rotatory powers of the above four acids and of *d*- α -hydroxybutyric, *l*- α -hydroxyisovaleric, *d*- α -hydroxyisohexaic, *d*- α -hydroxy- β -phenylpropionic, and *d*- α -hydroxyglutaric acids and their derivatives indicate that all these acids possess the same relative configurations, and they are designated as "*d*"-acids. Of the naturally occurring α -amino-acids, it is similarly assumed that *d*-alanine, *l*-serine, *l*-aspartic acid, *d*-valine, *l*-leucine, *d*-isoleucine, *d*- α -aminobutyric acid, *d*-glutamic acid, *l*-phenylalanine, and *l*-tyrosine all possess the same configurations, denoted by the symbol "*l*." The dextrorotatory (*d*-) α -halogen acids which have been isolated are assumed to be configuratively similar compounds and related configuratively to the "*l*"-amino-acids, which it is suggested are enantiomorphously related to the "*d*"-hydroxy-acids. This is supported by a comparison of the rotatory powers of the optically active α -bromoacylamino-acids with those of the α -aminoacylamino-acids. W. G.

The Radioactivity of the Waters of Neuchâtel and Seeland. H. PERRET and A. JAQUEROD (*Arch. Sci. phys. nat.*, 1918, [iv], **45**, 277—297, 336—348, 418—437).—The content in

radium emanation of the spring waters in a very small region, the Neuchâtel Jura mountains and neighbourhood, has been exhaustively studied. Then a minute parallel study of two regions, each of only a few square kilometres, and, lastly, the prolonged parallel study of two springs in the same district and then in different districts, were carried out. More than a hundred springs were examined. The radioactivity of these springs is feeble and varies between 0 and 3.5×10^{-10} curie of emanation per litre, the quantity varying in all the springs considerably with the time. No relation was found between radioactivity and the volume of flow of the spring or its temperature, and the few thermal and mineral springs found were not especially radioactive. In passing across the Jura chain from S.E. to N.W., there is a marked increase in the radioactivity of the water. The crystalline rocks beneath come nearer to the surface in travelling in this direction. The two springs examined continuously showed maxima and minima of radioactivity recurring at the same intervals of time. The quantity of radioactive salts in the waters was too small to be detected.

F. S.

Sign of the Zinc Electrode. WILDER D. BANCROFT (*J. Physical Chem.*, 1918, 22, 371—379).—A theoretical paper in which the sign given to potential values is discussed. It is pointed out that with electrodes which form cations, the *E.M.F.* is a measure of the difference of the chemical potentials, but has the opposite sign; with electrodes which form anions, the two potentials have the same sign. Since the electrical potential of the copper in a Daniell cell is higher than that of the zinc, and since the zinc electrode is the place of lowest electrical potential, although highest chemical potential, it follows that the minus sign ought to be used when writing the potential difference $\text{Zn}|\text{ZnSO}_4$. This is in keeping with the practice of physicists and physical chemists.

J. F. S.

Photochemical Cell, containing Complex Cyanides of Nickel or Platinum. SATOYASU IMORI (*J. Tokyo Chem. Soc.*, 1918, 39, 1—13).—A photochemical cell was constructed with platinum electrodes, which were immersed in a solution of potassium nickel cyanide or potassium platinocyanide, one only of the electrodes being exposed to light. In this cell the electrode exposed to light is positive, but in a photochemical cell containing a solution of potassium ferrocyanide, previously described by the author (*ibid.*, 1917, 38, 507), it was negative. The current from the present cell decays rapidly when the circuit is closed, notwithstanding the insertion of a considerable resistance, but in the former cell a constant current was obtained during the exposure to light. The cause of the *E.M.F.* of this cell is not yet known with certainty, but it would seem not to be the photoelectrical effect on the electrode, as it is not observed when the complex cyanides are replaced by other salt solutions.

S. H.

Method for Determining the Temperature of Luminous Flames. HERMANN SENFTLEBEN and ELISABETH BENEDICT (*Physikal. Zeitsch.*, 1918, 19, 180—181).—The temperature of luminous flames is obtained by inserting thin platinum or gold wires into the flame and estimating the temperature of the wires by means of a Holhorn-Kurlbaum pyrometer. To compensate for the loss of temperature occasioned by the insertion of the wire, it is raised to the temperature of the flame by the passage of an electric current. When the wire and flame are exactly at the same temperature there is no deposition of carbon, but if the temperature of the wire is lowered slightly there is an immediate deposition of carbon. To correct, if necessary, for the change of temperature brought about by change in the shape of the flame owing to the insertion of the wire, measurements were made with wire of varying diameters (0.2—1.0 mm.), and it was shown that only at greater diameters than these does the temperature depend on the thickness of the wire. The temperature of the middle of a Hefner lamp flame determined by this method is found to be 1690° abs., which is about the mean of the previously recorded values (1680 — 1711°). J. F. S.

Improved Form of Thermo-regulator. JOHN B. FERGUSON (*J. Amer. Chem. Soc.*, 1918, 40, 929—930).—The adjustment of the level of the mercury in the regulator tube is made by means of a plunger, and the mercury makes contact with a fixed platinum wire. H. M. D.

Thermo-regulator for Apparatus fitted with a Constant Water-level. JAROSLAV MILBAUER (*Zeitsch. anal. Chem.*, 1918, 57, 162—164).—The overflow water from the apparatus is conducted into one limb of a U-tube, the lower part of which is constricted and filled with mercury; the excess of water leaves the upper end of the limb of the U-tube through a side tube, a small by-pass being also fitted at the lower part of the limb. The other limb contains a floating valve, the lower end of which rests on the surface of the mercury. Should the supply of water be interrupted, the limb of the U-tube empties through the by-pass, decreasing the pressure on the mercury, and the valve falls, thus cutting off the supply of gas to the burner under the apparatus. W. P. S.

Cineole as a Solvent in Cryoscopy. CHARLES E. FAWSITT and CHRISTAIN H. FISCHER (*J. Roy. Soc. New South Wales*, 1918, 51, 467—472).—Cineole is an oil of the formula $C_{10}H_{18}O$ which occurs largely in oil of eucalyptus. It is extracted by simple freezing. This substance has h. p. 175 — 176° , m. p. 0.9° , it is very hygroscopic, and the presence of water in the product accounts for the m. p. -1° usually given. Cineole is not generally useful as a cryoscopic solvent, chiefly on account of its hygroscopic properties, but in some cases it is found to be a more suitable solvent than benzene, although somewhat more difficult to work with. It has a cryoscopic constant 6.7 and a latent heat of fusion 22.2 cal. per gram. J. F. S.

The Saturated Vapour Processes of Penta-atomic Substances. E. ARIÈS (*Compt. rend.*, 1918, **166**, 935—939).—Taking Young's values for the physical constants of stannic chloride, the author deduces the formula $\Pi = \tau^{20/7} Z / r$, where

$$r = \{1 + (1 - \tau)(0.84 - \tau) / [1.8(1 - \tau)^2 + 0.9]\} \tau^{13/7}$$

for the saturated vapour pressures of penta-atomic substances. The values calculated from this formula for methyl fluoride are in fairly close accord with those observed by Collie, except at a temperature of -5° . There is not such close agreement in the case of chloroform with the values as obtained by Regnault unless the critical constants of chloroform are taken as 247° and 45.26 atmos.

W. G.

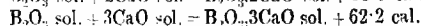
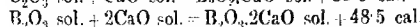
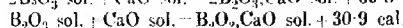
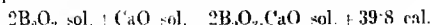
Rapid Pressure Method for the Determination of Molecular Weights and Hydrogen Equivalents. W. H. CHAPIN (*J. Physical Chem.*, 1918, **22**, 337—344).—A modification of the vapour density method of determining molecular weights by measuring the pressure set up by a known weight of vapour in a known volume at a measured temperature. The apparatus used consists of a 500 c.c. distilling flask the side tube of which is replaced by a mercury manometer. The manometer tube is 5 mm. diameter and 20 cm. high, and is fitted with a sliding celluloid scale. The top of the flask is fitted with the usual device for dropping in the substance at the right moment. The method is available for all liquids boiling below 90° . The substance is volatilised by steam, and as the whole of the apparatus is not at a uniform temperature, the average temperature must be computed. A method for deducing the average temperature is indicated. The usual precautions are taken in making the pressure measurement. An interesting innovation is introduced in the use of gelatin capsules for weighing the substance under investigation.

The same apparatus can be used for the determination of the equivalents of the metals zinc, aluminium, sodium, calcium, and magnesium. In all cases except sodium, weighed quantities of the metals are dropped into a measured volume of N — $3N$ -hydrochloric acid contained in the bulb of the apparatus; with sodium, alcohol is used.

J. F. S.

Heat of Formation of the Anhydrous Calcium Borates.

R. GRIVEAU (*Compt. rend.*, 1918, **166**, 993—995).—The pure anhydrous calcium borates were prepared by adding the calculated quantity of calcium carbonate to fused boric anhydride. The heat of solution of each of these borates in $N/2$ -hydrochloric acid was then determined, and from these results the heat of formation of each borate was calculated, the results obtained being given by the equation:



The energy of combination of each successive molecule of calcium oxide with two molecules of boric anhydride diminishes from 39.8 cal. to 13.7 cal.

W. G.

Apparatus for Cleansing Pyknometers. MARCEL DUGARDIN (*Ann. Chim. anal.*, 1918, **23**, 125-126).—A narrow glass tube, connected with a flask and a water-pump, is passed down the neck of the pyknometer so that the contents of the latter may be drawn off; water is then admitted to the pyknometer and drawn off again by means of the narrow tube.

W. P. S.

Adsorption Compounds. R. HALLER (*Kolloid Zeitsch.*, 1918, **22**, 113-133).—The formation of adsorption compounds by the interaction of dyes with other substances has been examined. Towards chemically indifferent solvents, adsorption compounds behave like mechanical mixtures. Adsorption compounds with a colourless adsorbent when dissolved in a suitable solvent show the same absorption spectrum as the corresponding solution of the dye. The melting points of adsorption compounds containing an adsorbent of low melting point are not very different from the melting point of the adsorbent. The general physical behaviour of the so-called adsorption compounds leads, therefore, to the conclusion that these are to be regarded as mechanical mixtures. [Compare *J. Soc. Chem. Ind.*, 411A.]

H. M. D.

Certain Relations between Crystalline Form, Chemical Constitution, and Optical Properties in Organic Compounds. EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1918, **8**, 277-285, 319-327).—In the expectation that there should be discoverable some relationship between the optical and the geometrical constants of crystals, an investigation has been made of a number of organic substances typical of the different classes of the tetragonal system. Making use of the Lorentz-Lorenz expression $(n^2-1)/(n^2+2)$, the author calculates refractivity constants R_o and R_i for the two principal refractive indices ω and ϵ , and finds that, in a number of cases, the ratio of these constants is almost exactly equal to the reciprocal of the crystallographic axial ratio in the corresponding directions in the crystal structure. Thus in the case of carbamide (tetragonal scalenohedral), $R_o/R_i = 0.834$, $a:c = 0.833$; in pentaerythritol (ditetragonal pyramidal), $R_o/R_i = 1.07$, $a:c = 1.024$; and in mellite, $C_6(CO_2)_6Al_2 \cdot 18H_2O$ (ditetragonal bipyramidal), $R_o/R_i = 1.046$, $a:c = 1.055$. A similar relation holds in the double propionates of calcium with strontium and lead, and in isomorphous mixtures of the latter with the corresponding cubic calcium-barium double salt. It is pointed out that the refraction ratios, as well as the crystallographic axial ratios, are connected with the spacing of the planes of atoms in the space-lattices of the substances, and that comparison of the two ratios may be expected to throw light on the type of space-lattice represented in each case. Skeleton space-lattices are suggested for the above-mentioned substances. A

number of exceptions to the rule of inverse proportionality occur. In some cases the deviation is due to an incorrect choice of axial ratios; in others it may be attributed to the presence of asymmetric carbon atoms or to atomic anisotropism. E. H. R.

Liquid Crystals of the Hydrates of 10-Bromophenanthrene-3- or -6-Sulphonic Acid. O. LEHMANN (*Ann. Physik.*, 1918, [iv], 55, 81—102).—In the solid state, the compound forms thin leaflets belonging apparently to the rhombic system, only slightly soluble in hydrochloric acid, from which it was recrystallised, easily soluble in alcohol, but with decomposition and separation of slender needles. The compound forms two liquid crystalline hydrates with water, the one with little water being slimy or gelatinous, that with more water forming separate liquid crystalline drops. The two forms appear to form mixed crystals to a limited extent. The liquid drops have been examined microscopically in great detail, both with ordinary and polarised light, and numerous diagrams are given illustrating the appearance of the drops under different conditions. The observations are held to support the author's theory of the molecular isomerism of the different modifications of a substance, as opposed to other theories of the relationship between amorphous and crystalline forms. E. H. R.

Colloidal Phenomena and the Adsorption Formula. JOHN A. WILSON and WYNNARETTA H. WILSON (*J. Amer. Chem. Soc.*, 1918, 40, 886—895).—The theory of the mechanism of protein swelling put forward by Procter and Wilson (*T.*, 1916, 109, 307) is further developed, and the commonly used empirical adsorption formula is discussed in relation to the theory.

It is shown that chemical combination of a colloid jelly with an electrolyte to form an ionised colloid salt will cause the jelly to swell to a maximum, which is followed by a gradually increasing contraction as the concentration of the electrolyte in the solution is increased. If an electrolyte which does not combine with the protein is added to the system, contraction of the swollen jelly takes place to an extent which depends on the resulting ionic concentration.

It is further shown that if the chemically combined electrolyte and the total quantity of electrolyte in the jelly are represented as functions of the concentration of the electrolyte in the external solution, curves are obtained which are of the same form as those which correspond with the empirical adsorption formula.

The microscopic pores found in certain hardened jellies are considered in relation to the continuity of the jellies regarded as two-phase systems. H. M. D.

Water-in-Oil Emulsions. ALFRED ULRICH MAX SCHLAEFFER (*T.*, 1918, 113, 522—526).—With the aid of finely divided carbon as emulsifier, it is possible to make emulsions of water in kerosene, turpentine, benzene, toluene, and other liquids which wet the solid

more readily than water does. The results of experiments with varying proportions of kerosene and water are described, and it is shown that the viscosity of the emulsions increases with the amount of water which they contain. In no circumstances was it found possible to obtain emulsions with water as the external phase. The emulsifying action of the carbon depends on the fact that the oil-wetted carbon particles form a skin over the water droplets, and thus prevent their coalescence.

Carron oil is an emulsion of the water-in-oil type, and mixes freely with organic solvents, but not with water without shaking.

H. M. D.

Equilibrium in the System: Ferrous Carbonate, Carbon Dioxide, and Water. HERBERT J. SMITH (*J. Amer. Chem. Soc.*, 1918, **40**, 879—883).—The solubility of ferrous carbonate in aqueous solutions of carbonic acid of varying concentration has been measured at 30°. The experiments were carried out in a steel bottle, which was agitated for several days to ensure the attainment of equilibrium. The ferrous carbonate was prepared by the interaction of equimolecular quantities of ferrous sulphate and sodium hydrogen carbonate at 100° in aqueous solution saturated with carbon dioxide at a pressure of about 30 atmospheres.

The concentrations of the dissolved ferrous salt and carbon dioxide are found to satisfy the relation

$$\alpha[\text{Fe}(\text{HCO}_3)_2]/\sqrt{[\text{H}_2\text{CO}_3]} = K,$$

in which α represents the degree of ionisation of the ferrous hydrogen carbonate, which has been assumed to be the same as that of barium nitrate in equivalent concentration. The average value of K is 4.04×10^{-3} . Since the above theoretical constant $K = 2/K_1K_3/4K_2$, where K_1 and K_2 are the first and second ionisation constants for carbonic acid and K_3 is the ionic solubility product for ferrous carbonate, it is possible to calculate K_3 . Putting $K_1 = 3.75 \times 10^{-7}$ and $K_2 = 4.91 \times 10^{-11}$, this equation gives $K_3 = 34.53 \times 10^{-12}$. From this it follows that, in the absence of hydrolytic decomposition, the solubility of ferrous carbonate in pure water would be 5.8×10^{-6} gram-molecules per litre.

H. M. D.

Equilibrium in the System: Zinc Carbonate, Carbon Dioxide, and Water. HERBERT J. SMITH (*J. Amer. Chem. Soc.*, 1918, **40**, 883—885).—The experiments were carried out in exactly the same way as those referred to in the preceding abstract. The zinc carbonate was prepared from the purest commercial product, which was treated with successive large quantities of boiling water. The basic carbonate was then subjected to the prolonged action of an aqueous solution of carbon dioxide under a pressure of about 30 atmospheres.

The quantities of zinc carbonate dissolved by carbonic acid solutions of varying concentration at 25° and 30° are in agreement

with the formula $\alpha[\text{Zn}(\text{HCO}_3)_2] / \sqrt{[\text{H}_2\text{CO}_3]} = 3.36 \times 10^{-2}$, where α is assumed to have the same value as for zinc chloride.

From this value of the equilibrium constant and the ionisation constants for carbonic acid, the ionic solubility product, $K_s = [\text{Zn}^{++}][\text{CO}_3^{--}]$, is found to be 21×10^{-12} at 25° . In the absence of hydrolysis, the solubility of zinc carbonate in pure water at 25° would therefore be 4.58×10^{-6} gram-molecule per litre.

H. M. D.

Application of the Mass Law to the Process of Disinfection, being a Contribution to the Mechanistic Theory as Opposed to the Vitalistic Theory. RICHARD EDWIN LEE and C. A. GILBERT (*J. Physical Chem.*, 1918, **22**, 348—372).—An historical account of the development of the existent theories of disinfection is given, and the various theories, grouped into the two classes vitalistic theories and mechanistic theories, have been subjected to criticism in the light of data accumulated by a number of workers, obtained independently in many places and from some new experimental data of the authors. The velocity of disinfection has been determined in the case of *Bacillus typhosus* with phenol at 37.5° , anthrax spores with mercuric chloride at 20° , and *Staphylococcus pyogenes aureus* with phenol at 20° . In all cases, the disinfectant had a concentration of 0.2%. The velocity of reaction was determined by a modification of the Rideal-Walker drop method. A suitable quantity of the diluted broth culture of the micro-organism under examination was put into a test-tube containing a quantity of disinfectant solution of known concentration, and then placed in an incubator. After successive definite time intervals, accurately measured portions were transferred to Petri dishes and "plated," incubated, and the surviving organisms counted. The authors are of the opinion that the experimental evidence makes it probable that disinfection is an orderly time process which is closely analogous to a chemical reaction, the micro-organisms and the disinfectants being regarded as the respective reagents. A definite logarithmic relationship between velocity of disinfection and concentration has been found to exist in all cases investigated. Confirmation of the foregoing is furnished by the fact that the velocity of disinfection is influenced by variations in temperature and concentration in a manner in accord with the mass law. The explanation why disinfection is not sudden, but takes place according to the mass law, is as follows. Owing to changes in bacterial constituents, only a certain number of individuals are in a condition to be attacked by the disinfectant at a given time, but the total number of individuals in such a condition at any given moment represents a constant proportion of the surviving micro-organisms. The author considers the objections to the mechanistic theory put forward by Reichenbach (*Zeitsch. Hygiene*, 1910, **10**, 237), and points out that it is not necessary to regard disinfection as a reaction of the first order, but rather, as is pointed out by Nernst, as a reaction of a higher order. The

theory of graded resistance advanced by Eykman, Hewlett, and Reichel (A., 1909, ii, 1045; *Biochem. Zeitsch.*, 1908, 11, 12) is criticised, and it is shown that the biological characteristics are distributed as a rule in a manner quite different from that assumed in the formation of the theory. In view of these observations, the authors are led to the conclusion that the logarithmic nature of disinfection is due to a general similarity of the individuals in a given pure culture rather than to a dissimilarity of the individuals as postulated in the theories of graded resistances by the supporters of the vitalistic theory. The authors also point out that although the work of Chick and Martin, and of Browning and Gilmour (*J. Path. and Bact.*, A., 1913, i, 1138), indicates the specificity of disinfectants, this behaviour is to be expected if the disinfection process is analogous to chemical action, for in the application of the principle of the mass law the influence of the affinity factor is always taken into account.

J. F. S.

Catalysis. IX. Calculation in Absolute Measure of Velocity Constants and Equilibrium Constants in Gaseous Systems. WILLIAM CUDMORE McCULLAGH LEWIS (T., 1918, 113, 471—492).—The concept of critical energy and critical increment in connexion with the formation of active molecules is further considered, and it is shown that reaction velocities and equilibrium constants may be calculated on the basis of molecular statistical considerations. Expressions are derived for the velocity of a unimolecular reaction and of bimolecular reactions in which the reacting molecules are of the same kind and also of different kinds. The theoretical treatment includes a consideration of the reaction velocity formulæ in the light of the radiation hypothesis.

The formulæ derived are applied to a number of gaseous reactions which have been experimentally examined, such as the decomposition of hydrogen iodide, the combination of hydrogen and iodine, and the dissociation of iodine, bromine, chlorine, and hydrogen, and it is shown that the calculated results are in fair agreement with those found by experiment. The formulæ may be used for the calculation of velocity or equilibrium constants in regions which do not admit of experimental determination by reason of the extremely high or low velocities which are involved.

The question of the unimolecular decomposition of hydrogen iodide is discussed, and it is shown that the velocity is very small compared with that of the bimolecular change at all temperatures at which this reaction has been examined experimentally. Calculation indicates, however, that the two velocity constants should be of the same order of magnitude in the neighbourhood of 1200° (abs.). At this temperature, the progress of the reaction would consequently not be satisfactorily represented by the equation for a bimolecular change.

H. M. D.

Periodic System of the Elements. STEFAN MEYER (*Physikal. Zeitsch.*, 1918, 19, 178—179).—The author gives two methods of

representing the periodic classification, in the first of which each series is written out at length and arranged in such a way that the eighth group elements lie in the centre of the scheme; to the right the elements of groups 1, 2, 3, etc., in order, and to the left the elements 7, 6, 5, etc. This arrangement places the elements of smallest atomic volume in the centre, so that passing either to the left or right of the centre is accompanied by an increase of atomic volume. In the second arrangement, the alkali metals occupy the middle of the table; to the right the groups follow 2, 3, 4 . . . 8, with + valencies 2—8, and to the left the groups 0, 7, 6 . . . 1, with -valencies 0—7. This arrangement places the elements with largest atomic volume in the centre, and on passing either to the right or left of the centre there is a decrease in atomic volume. The author places both the atomic weights and the atomic numbers alongside the elements. In the first arrangement, the elements of the rare earth group are placed together in groups III and IV to the left of the table, whilst in the second arrangement they are spread out in various groups in the third and fourth long series, although in this case the author definitely states that their positions are not definitely fixed. J. F. S.

The "De-salting" of Sea-water. WALTER BRIEGER (*Chem. Zeit.*, 1918, 42, 302. Compare A., 1911, ii, 723).—Quotations are given from ancient and modern literature to show that sea-water is not freed from salt by passing it through porous earthenware, as stated by Aristotle. W. P. S.

New Simple Ultra-filters. II. Spontaneous Ultra filters. WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1918, 22, 143—147. Compare this vol., ii, 192).—The efficiency of the ultra-filters which have been previously described has been found to depend on the presence of moisture in the filter paper which is used in the preparation of the filters. Dry filter paper does not give nearly such satisfactory results as filter paper which contains appreciable quantities of moisture. By treatment of moist filter paper with 2% collodion solution in the manner previously described, ultra-filters are obtained which show a markedly increased rapidity of action. Such ultra-filters may be used without the application of external pressure as an aid to filtration. The observed differences in the efficiency of ultra-filters made with dry and moist filter paper are attributable to differences in the structure of the collodion membrane in the two cases. The greatly increased filtering surface which is obtained when moist filter paper is used may be accounted for in terms of the structural peculiarities which are exhibited by the collodion membrane formed at the surface of water. H. M. D.

Simplified Short Vacuum Gauge. ENOCH KARRER (*J. Amer. Chem. Soc.*, 1918, 40, 928—929).—A modified short Gaede gauge is described in which the connexion between the adjustable mercury receiver and the exhausted space is made through a steel tube

which is welded to a tube of platinum foil, which in turn is fused into the lower end of the glass gauge tube. This is silvered and then copper-plated, and the seam in the platinum foil is then rendered gas-tight by a layer of solder bridging the copper-plated glass surface and the surface of the steel tube.

H. M. D.

Inorganic Chemistry.

Hydrogen Ion Concentrations of Various Indicator End-points in Dilute Sodium Hypochlorite Solutions. GLENN E. CULLEN and J. HAROLD AUSTIN (*J. Biol. Chem.*, 1918, **34**, 553—568).—The end-points of indicators in dilute sodium hypochlorite solutions are different from the end-points of the same indicators in ordinary solutions, on account of the bleaching action of the hypochlorite. The end-point to powdered phenolphthalein in a 0.5% sodium hypochlorite solution is at a P_H of about 10.1, whilst in an alcoholic solution of *o*-cresolphthalein it is at a P_H of about 9.3. The latter indicator gives an end-point in 1% sodium hypochlorite solution at about P_H 9.6. In the preparation of Dakin's hypochlorite solution (*A.*, 1915, i, 924), the authors recommend that chlorine should be passed into a sodium carbonate solution containing 14 grams to the litre until sodium hypochlorite is formed in a concentration of 0.5%, as shown by titration with thiosulphate.

H. W. B.

Absorption of Atmospheric Gases by Water. II. A Diagram showing the Volume of Oxygen dissolved by Water at Different Temperatures and Pressures. Additions to the Bibliography. J. H. COSTE (*J. Soc. Chem. Ind.*, 1918, **37**, 170—171r. Compare *A.*, 1917, ii, 463).—To facilitate the calculation of the volume of oxygen dissolved in water, the author has constructed a series of graphs which give the number of c.c. of oxygen dissolved in 1 litre of water at temperatures from 0° to 25° and pressures from 710 mm. to 780 mm. An additional bibliography is added to the paper.

J. F. S.

Effect of Acetylene on the Oxidation of Ammonia to Nitric Acid. GUY B. TAYLOR and JULIAN H. CAPPS (*J. Ind. Eng. Chem.*, 1918, **10**, 457—459).—The presence of a small quantity of acetylene in the ammonia-air mixture has a deleterious effect on the platinum catalyst; with 0.02% of acetylene, the yield falls from 95% to 89% or less, whilst 0.1% of acetylene decreases the yield to 66%. Ammonia gas may be freed from acetylene and other non-reacting gases by dissolving it in water to form a concentrated solution and then vaporising the latter with air. [See, further, *J. Soc. Chem. Ind.*, August.]

W. P. S.

Density, Compressibility, and Atomic Weight of Argon. A. LEDUC (*Compt. rend.*, 1918, 167, 70—71).—Working with a carefully purified sample of argon, the author finds for its density the value 1.3787, for its coefficient of departure from Mariotte's law between 1 and 5 atmos., at 14° the value 10.2×10^{-6} , and for its atomic weight the value 39.91. W. G.

The Reaction between the Alkali Phosphates and Magnesium Chloride. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1918, 102, 241—246).—The author has examined the precipitates formed by bringing together under different conditions magnesium chloride and disodium, dipotassium, or dirubidium hydrogen phosphate. Generally, magnesium monohydrogen phosphate is precipitated, with a variable content of water of crystallisation, but it is liable to be contaminated with magnesium monoalkali phosphate, and under suitable conditions the whole of the precipitate may be formed of the latter type of salt. Thus, when a dilute solution of magnesium chloride is added slowly with agitation to a 10% solution of dipotassium hydrogen phosphate, the salt $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ is precipitated in an almost pure condition, but if the solutions are mixed in the reverse order, the precipitate is of uncertain composition, containing variable quantities of MgKPO_4 aq., MgHPO_4 aq., $\text{Mg}(\text{OH})_2$, and $\text{Mg}_3(\text{PO}_4)_2$. The rubidium salt, $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$, can be precipitated almost pure in a similar manner to the potassium salt.

The work of Fröschel has shown (*Ber. Südslav. Akad.*, 1912, 190, 117—138) that in whatever manner dilute solutions of magnesium chloride and disodium hydrogen phosphate are mixed, equilibrium between the products of reaction is eventually obtained. Fröschel omitted to observe, however, that the precipitate is not pure MgHPO_4 aq., but liable to be contaminated with magnesium alkali phosphate. The author quotes analyses showing that when saturated solutions of these salts are mixed, the precipitate contains a considerable quantity of alkali. The results explain the reason for the supposed existence of so many hydrates of MgHPO_4 , and also emphasise the danger of the presence of alkali cations during the estimation of phosphoric acid by the magnesium ammonium phosphate method. E. H. R.

Isotopic Lead. FRANK WIGGLESWORTH CLARKE (*Proc. Nat. Acad. Sci.*, 1918, 4, 181—188).—The constancy of the atomic weight of lead from non-radioactive minerals and its independence on the species and locality of the mineral suggest that ordinary lead is a distinct variety, not a balanced mixture of the isotopes derived from uranium and thorium. The very variable atomic weight of lead derived from uranium minerals suggests that this "normal" or ordinary lead is present in varying amount along with the isotope derived from uranium. A hypothesis of elementary evolution is suggested, in which ordinary lead is a product of evolution, the lighter elements condensing in the processes into the heavier

elements, and the isotopes formed in radioactive change are products of degradation or decay. The atom being a very highly complex structure, in which the constituents must come together in irregular proportions, the process of evolution from the lighter to the heavier forms is regarded as a slow process in which the final stable configuration is not at once attained, but only after a period of selection of the constituent parts. F. S.

Mercury Hydrosols produced from Metallic Mercury.

IVAR NORDLUND (*Diss., Uppsala*, 1918, 1--125).—The preparation of mercury sols has been studied by a variety of methods, which include (a) mechanical dispersion methods, (b) thermal dispersion methods, and (c) electrical dispersion methods. Under the first group of methods, it is shown that by spirting a fine stream of mercury by means of high pressure into solutions of potassium nitrate and gelatin, definite sols of mercury are produced, although the particles are relatively large. With solutions of ammonia, ammonium chloride, ammonium sulphate, or carbamide, or even pure water, no sol-formation occurred by this method. When mercury is shaken with pure water or with dilute solutions of potassium chloride, sodium chloride, potassium nitrate, potassium sulphate, copper sulphate, mercurous nitrate, or acetic acid, there is no formation of colloidal mercury, but if dilute solutions (ca. $10^{-4}N$) of ammonia, ammonium sulphate, ammonium chloride, calcium citrate, tartaric acid, potassium tartrate, carbamide, or gelatin are used, definite colloidal solutions are produced. Mercury sols are also produced by passing hot mercury vapour directly into water. Mercury sols can be readily prepared by the Bredig method of electrical dispersion, using either direct or alternating current. The law of Stokes is tested for the velocity of fall of a mercury drop through an 11% solution of water in glycerol, and the results show that within the limits of experimental error the law holds for this case. The various sols have been examined in connexion with the distribution of the particles. The sols have varying colours from grey to yellowish-brown and reddish-brown; to characterise the colour of the sols more exactly, the absorption spectrum has been determined over the range $\lambda = 253-263 \mu$. A number of experiments are described on methods of estimating the purity of the sols produced in different ways, the stability toward various electrolytes, and the stabilising action of electrolytes. From kataphoresis experiments, it is shown that the sols are all positively charged except those prepared in citrate and tartrate solutions, which are negatively charged. J. F. S.

The Chemistry of Quinquevalent Tungsten. OSCAR O:SON COLLENEBURG (*Zeitsch. anorg. Chem.*, 1918, **102**, 247—276).—By the reduction of tungstic acid or a tungstate in oxalic acid solution with tin, the author has succeeded in preparing soluble, fairly stable complex oxalates containing quinquevalent tungsten. These salts have been isolated in a pure condition, and from them other

compounds containing quinquivalent tungsten have been prepared. The reduction with tin proceeds smoothly only in the one stage. It is best to reduce a solution of an alkali tungstate in a concentrated solution of oxalic acid containing slight excess of alkali oxalate. The course of the reduction can be followed by the colour change, through dark blue, green, and yellow to deep red. After removal of tin and excess of oxalic acid, the complex oxalate is precipitated by means of alcohol, and can be purified by dissolving in hot water and salting out, the sodium salt with sodium bromide, the potassium salt with potassium iodide. The compounds must be dried in a current of carbon dioxide, but are fairly stable in air when dry. The sodium salt has the composition $3\text{Na}_2\text{O} \cdot 2\text{W}_2\text{O}_5 \cdot 4\text{C}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$, and the potassium salt $3\text{K}_2\text{O} \cdot 2\text{W}_2\text{O}_5 \cdot 4\text{C}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$.

They are red, crystalline powders which slowly oxidise in air, and at 100° lose their water, but do not decompose. They are very soluble in water, insoluble in organic solvents. Sodium hydroxide in the cold precipitates from their aqueous solution a brown, amorphous substance containing quinquivalent tungsten, but on boiling, part of this dissolves to form a tungstate, whilst a dark residue remains, probably containing quadrivalent tungsten. The complex oxalates can be regarded as *oxalotungstites*, derived from a hypothetical tungstous acid.

The oxalotungstites dissolve in concentrated hydrochloric acid, forming a deep blue solution, which contains an *oxychloride* of quinquivalent tungsten, probably WOCl_3 . From this solution, complex chlorides can be isolated containing WOCl_3 in combination with chlorides of the alkali metals or ammonium or hydrochlorides of organic bases. The ammonium and potassium salts are precipitated by saturating a hydrochloric acid solution of the corresponding oxalotungstite with hydrogen chloride. The rubidium, caesium, aniline, tetraethyl- and tetrapropyl-ammonium compounds are precipitated when the corresponding chloride is added to a hydrochloric acid solution of an oxalotungstite, and the pyridine and quinoline compounds are prepared by double decomposition of their hydrochlorides with ammonium chlorotungstite. Four types of complex chlorides have been observed. Type Ia has the composition M_2WOCl_3 , in which M may be NH_4 , Rb, Cs, or $\text{C}_6\text{H}_5\text{NH}_3$; type Ib, $\text{M}_2\text{WOCl}_3 \cdot x\text{H}_2\text{O}$, is represented by the potassium compound; type IIa, MWOCl_4 , is represented by the pyridine and quinoline compounds, and type IIb, $\text{MWOCl}_4 \cdot \text{H}_2\text{O}$, by tetraethyl- and tetrapropyl-ammonium compounds. The compounds of type I correspond with the so-called molybdenyl chlorides; they form green crystals. Those of type II have no representative among molybdenum compounds; they form shining, brown crystals (IIa) or bright, greenish-blue crystals (IIb). The latter hold their water with great tenacity, and may be regarded as hydroxy-compounds, for example, $(\text{C}_6\text{H}_5)_4\text{N} \cdot \text{W}(\text{OH})_5\text{Cl}$. The author prefers to regard the compounds as chloro-derivatives of tungstous acid, rather than as double chlorides or tungstyl chlorides.

those of type II being derived from *metatungstous acid*, WO_2OH , and those of type I from the hydroxide, $\text{W}(\text{OH})_6$.

The *chlorotungstites* are stable in dry air at the ordinary temperature, but decompose with oxidation to tungstates at $60-70^\circ$. They are immediately hydrolysed by water with formation of a brown hydroxide, which has not been analysed. The less soluble cesium compound is, however, far more stable than the readily soluble ammonium and potassium compounds. They dissolve readily in absolute methyl and ethyl alcohols, with the exception of the rubidium and cesium compounds, but not in other organic solvents. Concentrated hydrochloric acid and 35% sulphuric acid also dissolve them, but alkalis and ammonia decompose them. Oxidising agents convert them into tungstates, and permanganate and iodine have been employed for quantitative determinations of the quinquevalent tungsten.

The chlorotungstites react vigorously with a concentrated solution of potassium cyanide with evolution of hydrogen cyanide. A reddish-yellow solution is formed containing cyanides of the type $\text{M}_x\text{W}(\text{CN})_6$, from which a sparingly soluble cadmium compound, $\text{Cd}_2\text{W}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$, has been isolated. A thiocyanic acid compound has also been isolated in the form of a pyridine salt having the composition $(\text{PyH})_2\text{WO}(\text{SCN})_6 \cdot x\text{H}_2\text{O}$.

Full details for the preparation of each of the chlorotungstites described are given.

E. H. R.

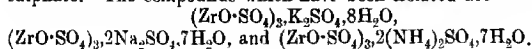
Behaviour of Solutions of Stannic Fluoride. N. HOWELL FURMAN (*J. Amer. Chem. Soc.*, 1918, 40, 906-914).—Stannic fluoride was prepared by the action of anhydrous hydrogen fluoride on stannic chloride according to the method of Ruff and Plato by the use of apparatus involving a minimum amount of platinum. According to observations on the electrical conductivity of its solutions, it hydrolyses much less rapidly than stannic chloride. The conductivity increases rapidly at first, but attains a constant value after some days. The final value corresponds closely with that calculated on the assumption that complete hydrolysis takes place in accordance with the equation $\text{SnF}_4 + 4\text{H}_2\text{O} = \text{Sn}(\text{OH})_4 + 4\text{HF}$.

Experiments made with a view to ascertain the amount of hydrofluoric acid which is necessary to prevent the precipitation of tin by the action of hydrogen sulphide show that the hydrogen ion concentration must be such that hydrolysis of the stannic fluoride becomes inappreciable. The anomalous behaviour of stannic tin in hydrofluoric acid solution may be explained either by the assumption that stannic fluoride has little tendency to ionise, or by the formation of complex ions of the type $\text{H}_n\text{SnF}_{4+n}$. Of the two hypotheses, the former seems to be in better agreement with the facts.

H. M. D.

Combinations of Normal Zirconyl Sulphate with some Alkali Sulphates ($\text{K}, \text{Na}, \text{NH}_4$). ED. CHAUVENET and (MLLE.) H. GUEYLARD (*Compt. rend.*, 1918, 167, 24-25. Compare this vol.,

ii, 234).—Normal zirconyl sulphate forms compounds of the types $(\text{ZrO} \cdot \text{SO}_4)_3 \cdot \text{X}$ or $(\text{ZrO} \cdot \text{SO}_4)_3 \cdot \text{X}_2$, where X may be ZrO_2 or an alkali sulphate. The compounds which have been isolated are



W. G.

Chemistry of Gold at High Temperatures and Pressures.

HAROLD H. MORRIS (*J. Amer. Chem. Soc.*, 1918, **40**, 917—927).

—In reference to the explanation of the occurrence of free gold in nature, experiments have been made on the behaviour of gold compounds under the influence of water at high temperatures and pressures. The experiments were made with a specially constructed steel bomb. Gold hydroxide yields metallic gold when treated with water at 322° . In presence of sodium chloride and magnesium chloride, decomposition takes place at a lower temperature; calcium chloride, on the other hand, tends to prevent the decomposition.

Gold chloride may be heated to the critical temperature (370°) before metallic gold appears. In presence of small quantities of sodium, magnesium, or calcium chloride, gold chloride is more stable, and reduction to the metal is not observed until the temperature is raised to 450 — 460° . The increased stability is attributed to the formation of double chlorides.

Calcite and magnesite become plated with gold when heated with gold chloride solutions up to 310° . Sodium, magnesium, and calcium chlorides prevent this action from taking place until the temperature is raised to about 500° .

Magnesium hydrogen carbonate acts like the normal carbonate, but calcium hydrogen carbonate appears to have no influence on the stability of a gold chloride solution.

It has also been observed that gold dissolves in hot hydrochloric acid containing auric chloride. Aurous chloride is formed.

H. M. D.

Mineralogical Chemistry.

The Constitution of Coal. MARIE C. STOPES and R. V. WHEELER (*Dept. Sci. Ind. Research*, 1918, 1—58).—A monograph in which the subject is dealt with both from the economic and scientific points of view. The points considered are the definition of coal and its general constitution, the principal methods of accumulation of coal-forming vegetable material, the action of solvents on coal, the destructive distillation and distillation at different temperatures, the nature of the liquid distillates, the microscopical evidence on the constitution of coal, the nature of

the "ulmic substances," the action of reagents on coal, and the nature of artificial coals. There is a brief discussion of the various theories on the constitution of coal, an appendix on the classification of coals, and a very full bibliography.

W. G.

Augite from Stromboli. S. KOZU and H. S. WASHINGTON (*Amer. J. Sci.*, 1918, [iv], **45**, 463-469).—Dull, black, or brownish-black crystals of augite about 1 cm. long occur loose in some abundance in the volcanic ash around the crater of Stromboli. D^{20}_{Na} 3.243. The refractive indices (α_{Na} = 1.693, β = 1.699, γ = 1.719) are lower than are usual for augite, corresponding with the preponderance of the diopside molecule shown by the following analysis. This analysis (I) corresponds with $\text{Ca}(\text{Mg}, \text{Fe})\text{Si}_2\text{O}_6$ 80.12, $(\text{Mg}, \text{Fe})\text{SiO}_3$ 7.48, $(\text{Mg}, \text{Fe})\text{Al}_2\text{SiO}_6$ 7.03, $\text{NaFeSi}_3\text{O}_8$ 5.46%. Analysis II is of the basalt scoria in which the crystals occur.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	NiO.	MgO.
I. 50.94	0.96	3.37	2.05	7.41	0.10	n.d.	14.59	
II. 50.83	0.81	16.66	1.52	6.64	0.12	n.d.	6.08	

	CaO.	SrO.	Na ₂ O.	K ₂ O.	P ₂ O ₅ .	H ₂ O.	Total.
I. 20.34	0.08	0.61	0.18	—	0.08	100.71	
II. 10.99	—	2.66	2.05	1.61	0.36	100.33	

L. J. S.

Analytical Chemistry.

Universal Gasometer. JAROSLAV MILBAUER (*Zeitsch. anal. Chem.*, 1918, **57**, 161-162).—The apparatus described allows the gas contained in it to be delivered at any predetermined rate and constant pressure, the water being admitted through an adjustable constant-level device.

W. P. S.

Mercuric Oxide as a Standard for Volumetric Analysis. G. INCZE (*Zeitsch. anal. Chem.*, 1918, **57**, 176).—A reply to Rosenthaler (this vol., ii, 236). The author's method for using mercuric oxide differs from that described by Rosenthaler and Abelmänn.

W. P. S.

Estimation of Halogens, Sulphur, and Nitrogen in the Presence of Mercury. MAURICE FRANÇOIS (*Compt. rend.*, 1918, **166**, 1000-1003).—For the estimation of halogens, the mercury is removed by means of zinc turnings by the method previously described (compare this vol., ii, 276), but without using potassium iodide, all the filtrates and decanted liquids being kept and mixed,

and in this solution the halogens are estimated by means of silver nitrate in the usual manner.

For the estimation of sulphur, this is first converted into sulphate by oxidation with bromine in hydrobromic acid, and then the mercury and excess of bromine are removed by the addition of zinc turnings, the sulphur being estimated in the filtrate by precipitation as barium sulphate.

Nitrogen in the form of mercuriammonium or mercuriamino-compounds is estimated in the filtrate, after the removal of mercury by the method described (*loc. cit.*), by addition of alkali and distillation of the ammonia or amine into dilute hydrochloric acid and weighing as ammonium chloride or amine hydrochloride.

W. G.

Volumetric Estimation of Chlorine, Bromine, Cyanogen, and Mercury. EMIL VOTOČEK (*Chem. Zeit.*, 1918, 42, 271—272. Compare this vol., ii, 238).—The method described for the titration of chlorides may also be applied to bromides and cyanides, but not to iodides or fluorides; conversely, it may be used for the volumetric estimation of mercury. The insolubility of cupric nitroprusside affords a means of separating this metal from mercury, since mercury nitroprusside is soluble in the presence of an excess of sodium chloride. [See, further, *J. Soc. Chem. Ind.*, 444A.]

W. P. S.

Estimation of Combined Chlorine in Gastric Juice. GEORGES and FABRE (*Soc. Pharm. Paris*, 1917; from *Ann. Chim. anal.*, 1918, 23, 133—134).—Five c.c. of the sample are heated with 10 c.c. of *N*/10-silver nitrate solution, 6 c.c. of saturated potassium permanganate solution, and 10 c.c. of nitric acid; the excess of silver nitrate is then titrated with thiocyanate solution. This gives the total chlorine. Another portion of 5 c.c. of the sample is evaporated in a platinum basin, and the combined chlorine is estimated in the residue as described. The fixed (inorganic chlorine) is estimated in the ash of the sample. Three specimens of gastric juice contained 2.99, 2.84, and 1.09 grams of fixed chlorine per litre, respectively.

W. P. S.

Detection of Iodides in the Presence of Cyanides. L. J. CURTMAN and C. KAUFMAN (*J. Amer. Chem. Soc.*, 1918, 40, 914—917).—Comparative experiments made on the detection of iodide in presence of relatively large quantities of cyanide with potassium nitrite, potassium permanganate, hydrogen peroxide, and chlorine as oxidising agents show that the interference of cyanide is least when permanganate is used as the oxidising agent.

If the cyanides are precipitated by the addition of cobalt nitrate and the filtrate examined for iodide by the use of permanganate, sulphuric acid, and chloroform, it is possible to detect 1 part of iodide in presence of 500 parts of cyanide. [See *J. Soc. Chem. Ind.*, 413A.]

H. M. D.

The Microchemical Method of Estimating Residual Nitrogen. IVAR BANG (*Biochem. Zeitsch.*, 1918, 87, 259—263).—The urea can be first extracted from the blood sample on filter paper by treatment with alcohol-ether mixture for five hours, and the remaining nitrogen is then extracted with phosphomolybdic acid solution (0.05% phosphomolybdic acid + 1.5% sulphuric acid) for one hour. The nitrogen in each extract is estimated by the micro-Kjeldahl method. S. B. S.

Detection of Nitrates in Water. ESCAICH (*J. Pharm. Chim.*, 1918, [vii], 17, 395).—Fifteen c.c. of the water are mixed with 2 c.c. of 10% antipyrine solution and 4 drops of acid mercuric sulphate solution, and a drop of 5% potassium ferrieyanide solution is added. In the presence of 0.1 mg. of nitrite per litre of water, a red coloration is obtained. The reaction is characteristic of nitrites and may be used for the detection of nitrates after these have been reduced by "amalgamated" aluminium. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

Simplified Working with a Nitrometer. RUDOLF KAESFÖRER (*Chem. Zeit.*, 1918, 42, 296).—In the usual gasometric estimation of nitric acid, an approximate correction is made for the pressure due to the acid layer, a depth of 7 mm. of acid being taken as equivalent to 1 mm. of mercury. A more trustworthy procedure is to bring the mercury to the same level in the measuring and levelling tubes, read the volume of the gas, open the tap of the measuring tube, and note the difference in level of the mercury. This difference in mm. is subtracted from the barometric pressure during the experiment. W. P. S.

Estimation of Nitric Acid in Bismuth Subnitrate. E. LUCK (*Bull. Soc. chim.*, 1918, [iv], 23, 264—271; *J. Pharm. Chim.*, 1918, [vii], 17, 349—359).—At 95° bismuth subnitrate reacts with oxalic acid in the presence of manganese sulphate according to the equation $6(\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}) + 2(\text{BiO} \cdot \text{NO}_2) + \text{H}_2\text{SO}_4 = 2\text{NO} + 3\text{CO} + 9\text{CO}_2 + 19\text{H}_2\text{O} + (\text{BiO})_2\text{SO}_4$. About 0.5 gram of bismuth subnitrate and 1 gram of manganese sulphate are heated in a flask under a reflux apparatus for one and a-half hours with 50 c.c. of a solution containing 20 grams of crystallised oxalic acid and 60 c.c. of sulphuric acid per 100 c.c.; to prevent secondary reactions, a current of carbon dioxide must be passed through the flask during the reaction. The excess of oxalic acid is then titrated with standardised permanganate solution. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

Critical Elaboration of Quantitative Precipitation Methods Exemplified by a Method for the Estimation of Phosphoric Acid. H. HEIDENHAIN (*J. Ind. Eng. Chem.*, 1918, 10, 426—429).—To determine whether a method is trustworthy, it is necessary to know the solubility of the precipitate and the

influence of concentration, temperature, presence of other substances, etc. The purity of the precipitate also requires investigation. In the estimation of phosphoric acid by precipitation with molybdic acid and titration of the precipitate with sodium hydroxide solution, the presence of ammonia interferes with the end-point when phenolphthalein is used as the indicator. It is therefore recommended that the phosphoric acid should be precipitated as potassium phosphomolybdate and the precipitate washed with 10% potassium nitrate solution containing free nitric acid ($N/100$ strength). The small quantity of acid remaining in the filter can be estimated and a correction made. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

The Wet Method for Estimation of Carbon. WILHELM STEPP (*Biochem. Zeitsch.*, 1918, 87, 135—142).—The author discusses the following points in the wet estimation: (a) The form of the apparatus. This is figured in the text, and the flask in which decomposition takes place is connected with a condenser to retain the acid. (b) The purification of the sulphuric acid. This is accomplished by heating it first with potassium dichromate, and afterwards with permanganate. (c) The purity of potassium dichromate used for oxidation of organic salts. It is difficult to obtain this quite free from carbonate. The author substitutes a mixture of chromic acid and sulphuric acid. Finally, when oxidation with the mixture of chromic and sulphuric acids has gone on for four hours, the apparatus is allowed to cool in a current of air free from carbon dioxide, and 10 c.c. of 5% solution of potassium permanganate are added, and the mixture is heated for another hour. S. B. S.

The Estimation of Carbonates and Hydrogen Carbonates in the Cold; Analysis of a Mixture of these Salts. Exact Details for the Use of Litmus and Phenolphthalein as Indicators. W. MESTREZAT (*Bull. Soc. chim.*, 1918, [iv], 23, 250—254).—The author finds that in the titration of carbonates, using phenolphthalein as indicator, a satisfactory and correct end-point is obtained when the whole of the carbonate is just converted by the acid into hydrogen carbonate, if the alkaline liquid is so diluted as not to contain more than 0.07% of sodium carbonate.

Similarly, total alkalinity may be determined by titration in the cold, using litmus as an indicator, if the procedure used is as follows. The standard acid is run in, 1—2 c.c. at a time, until a change in the tint of the indicator is just noticeable. Then between each successive addition of 0.2—0.3 c.c. of acid the liquid is mixed and divided into two parts, one being used as a control and the other receiving the acid. That point at which an addition of acid produces no colour change, as shown by the comparison, is the end-point. W. G.

Estimation of Sodium and Potassium [in Foodstuffs, etc.]. S. N. RHUE (*J. Ind. Eng. Chem.*, 1918, 10, 429—431).—The

sulphated ash of the substance is dissolved in hydrochloric acid, and after separation of phosphoric acid, iron, calcium, magnesium, etc., the sodium and potassium are weighed together as sulphates. The potassium is estimated in a separated portion of the ash by precipitation as potassium platinichloride after the iron and calcium have been removed. The potassium platinichloride is washed with 80% alcohol, then with 20% ammonium chloride solution saturated with potassium platinichloride (this removes magnesium sulphate and traces of calcium salts), and finally with 80% alcohol. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

The Lawrence-Smith Method for the Estimation of Alkalis in Silicates. P. WENGER and ED. BRANGE (*Mon. Sci.*, 1918, [v], 8, I, 97—99).—The Lawrence-Smith reaction for the decomposition of silicates (heating with a mixture of calcium carbonate, 8 parts, and ammonium chloride, 1 part) is complete when the mixture is heated for two hours at 700°. After cooling, the mixture is treated with water, filtered, the calcium is removed from the filtrate, and the alkalis then estimated in the usual way. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

Detection of Strontium in the Presence of Barium by Calcium Sulphate Solution. THEODORA P. RAIKOW (*Zeitsch. anal. Chem.*, 1918, 57, 164—170).—Although strontium sulphate forms slowly when a soluble strontium salt is treated with calcium sulphate solution, the presence of a barium salt, and consequent formation of barium sulphate, greatly increases the rate of precipitation of strontium salt. To detect strontium in the presence of barium, 10 c.c. of the solution to be tested are treated with an excess of calcium sulphate solution, the mixture shaken for fifteen seconds, and then filtered. If the filtrate becomes turbid after a short time, or does so when boiled, strontium is present. In cases where a turbidity is not obtained, the precipitate on the filter should be washed several times with hot water and the filtrate now tested with barium chloride solution; the washing dissolves out any strontium sulphate precipitated with the barium sulphate, and a turbidity is produced on the addition of barium chloride. W. P. S.

Precipitation of Magnesium as Oxalate and the Theory of the Formation of Precipitates. A. ASTRUC and J. CAMO (*J. Pharm. Chim.*, 1918, [vii], 17, 381—386).—A discussion of the conditions affecting the precipitation of magnesium oxalate. The quantity of this oxalate which is precipitated from magnesium acetate solution by oxalic acid increases with the concentration of the acetate solution. In the separation of large quantities of magnesium salts from calcium salts, the calcium oxalate should be precipitated from a very dilute solution. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

Hæmatoxylin as a Reagent for Copper Ions and Imperfect Complexes of Copper. S. REBELLO-ALVES and A. BENEDICENTI (*Arch. farm. sper. sci. aff.*, 1917, **24**, 50—57; from *Physiol. Abstr.*, 1918, **3**, 164).—To detect the presence of copper in protein complexes, the solution is treated with a drop of neutral red solution and then with a very dilute solution of sodium carbonate until a clear yellow is obtained, when the solution is sufficiently alkaline for the reaction between hæmatoxylin and copper.
S. B. S.

The Titration of Copper with Potassium Cyanide. M. P. APPLEBEY and K. W. LANE (*Analyst*, 1918, **43**, 268).—In titrating copper with potassium cyanide, the end-point of the reaction is no longer sharp in the case of solutions containing much less than 1 gram of copper per litre. A method of titrating amounts of about 0.1 gram per litre, however, has been based on the fact that a solution of a double carbonate of copper and an alkali in excess of sodium carbonate solution reacts sharply with cyanide, the end-point of the reaction being shown by the colour changing from blue to an unstable grey, the solution becoming clear and colourless in a few minutes. The double carbonate is prepared by adding the copper solution to a solution of sodium carbonate and sodium hydrogen carbonate, the presence of the latter being necessary to prevent the precipitation of a basic carbonate.

C. A. M.

Volumetric Estimation of Copper by Potassium Thiocyanate, Potassium Iodide, and Thiosulphate. G. BRUNN (*Chem. Zeit.*, 1918, **42**, 301—302).—The presence of potassium thiocyanate is of advantage in the iodometric estimation of copper, since it decreases the amount of potassium iodide required. The cupric salt solution is treated with a small quantity of potassium iodide and then titrated with thiosulphate solution containing potassium thiocyanate. The latter reacts with the cuprous iodide first formed and liberates an equivalent amount of potassium iodide, which in turn reacts with a further quantity of the cupric salt. [See, further, *J. Soc. Chem. Ind.*, 446A.]
W. P. S.

A New Method of Estimating Mercury by means of Zinc Filings. MAURICE FRANÇOIS (*Compt. rend.*, 1918, **166**, 950—952).—The mercury salt, in a finely divided state, is placed in a conical flask with 1 gram of zinc filings and 10 c.c. of 2*N*-sulphuric acid. After half an hour, a second quantity of zinc and acid is added, this being repeated at the end of the first hour. After twenty-four hours, the liquid is decanted through a filter and the residue washed four times by decantation with water. To it is then added, 5 c.c. at a time, 25 c.c. of dilute hydrochloric acid (1:1). After twenty-four hours, this liquid is decanted and 25 c.c. of fuming hydrochloric acid are added. After a further twenty-four hours, the zinc has all dissolved, and the mercury is in

the form of one large globule, which is carefully washed by decantation, transferred to a porcelain crucible, and dried first by filter paper and finally over sulphuric acid in the cold, and weighed. The method is accurate and applicable to all mercury salts except the sulphide, which must first be oxidised to the sulphate. It is advisable to add 0.5 gram of potassium iodide to the mercury salt before commencing the estimation.

W. G.

The Use of Hydrofluoric Acid in Analysis. N. HOWELL FURMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 895—906).—A summary is given of the results which have been previously obtained by the use of hydrofluoric acid solutions in the separation of metals by electro-analysis and by precipitation as sulphides. Further results are given which show that copper can be quantitatively separated from vanadium in acid fluoride solution by electro-deposition of the copper. Vanadium thus behaves similarly to tin and tungsten, and preliminary observations indicate that uranium and titanium fall into the same category.

The general chemical behaviour of stannic tin in acid fluoride solutions shows that the stannic ion is not present in appreciable quantity, for such solutions give none of the characteristic reactions of stannic tin. In consequence of this behaviour, hydrofluoric acid may be conveniently used in the analysis of tin-antimony alloys. The procedure recommended is described in detail.

By the addition of boric acid to an acid fluoride solution of stannic tin, the ordinary chemical properties of the stannic ion are developed, and the tin may be quantitatively separated by the action of hydrogen sulphide or by electro-deposition. The boric acid may be replaced by silica with similar results. The action of the boric acid is presumably connected with the formation of borofluoride, and it is shown that acid fluoride solutions to which excess of boric acid has been added have comparatively little action on glass vessels.

The action of boric acid on the behaviour of tin in hydrofluoric acid solution is made the basis of a method for the qualitative analysis of the tin group of metals. [See also *J. Soc. Chem. Ind.*, 445A.]

H. M. D.

Colorimetric Estimation of Lactose in Milk. AUGUST J. P. PACINI and DOROTHY WRIGHT RUSSELL (*J. Biol. Chem.*, 1918, **34**, 505—507).—A modification of Lewis and Benedict's colorimetric method for the estimation of dextrose in the blood (*A.*, 1915, ii, 111) is described for the estimation of lactose in milk. [See, further, *J. Soc. Chem. Ind.*, August.]

H. W. B.

Nephelometric Values of Cholesterol and the Higher Fatty Acids. FRANK A. CSONKA (*J. Biol. Chem.*, 1918, **34**, 577—582).—The nephelometric value of a substance is defined by the author as the turbidity produced by a given amount of the substance compared in a nephelometer with a given standard

within a given length of time. Taking oleic acid as a standard, for example, the nephelometric values of cholesterol, stearic and palmitic acids, are all different, but the nephelometric value of a mixture of any two of them is the sum of the nephelometric values of the constituents. The nephelometric value is influenced by the concentration of acid in the suspension, and the degree of turbidity changes with varying rapidity with the lapse of time. For every substance there is an optimum acid concentration which produces the highest nephelometric value with the least change within a specified interval of time.

H. W. B.

The Colloid Chemistry of Fehling's Sugar Test. M. H. FISCHER and M. O. HOOKER (*J. Lab. and Clin. Med.*, 1918, **3**, 368—373; from *Physiol. Abstr.*, 1918, **3**, 181).—The varying colours produced by Fehling's solution are ascribed to the different sizes of the reduced copper oxide particles held in suspension.

S. B. S.

Physiology of Blood-sugar. I. Bang's Micro-method of Sugar Estimation. RICHARD EGE (*Biochem. Zeitsch.*, 1918, **87**, 77—91).—A revision of Bang's method, directing attention more especially to the influence of the time taken in reduction on the results. The following suggestions are made: (1) A longer time than that suggested by Bang ("Methode zur Microbestimmung einiger Blutbestandtheile," 1916). (2) The use of a gas-regulator (figured in text). (3) Strict adherence to standard methods. Attention is also directed to a source of error from the fact that certain substances acting on iodine can be removed from the indiarubber of the apparatus. Methods for avoiding this source of error are indicated.

S. B. S.

The Microchemical Method of Estimation of Blood sugar. IVAR BANG (*Biochem. Zeitsch.*, 1918, **87**, 248—258). The two chief errors in the author's method are due to differences in the intensity of boiling during the reduction, and to the oxidation by air during titration. The first of these can be overcome by passing the gas used for heating through a special form of valve, which is figured in the text, and the second by oxidising the reduced cuprous oxide by excess of potassium iodate and estimating the excess of iodate by titration. The solutions employed are the following: (1) Solution for coagulating the blood (weighed on filter paper by a torsion balance), 1360 c.c. of saturated solution of potassium chloride, 1.5 c.c. of 25% hydrochloric acid, 3 grams of uranyl acetate dissolved in 200 c.c. of water, and the mixture diluted to 2 litres. In this are dissolved 500 mg. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. (2) The iodate solution is made by dissolving 0.2230 gram of pure potassium iodate and 50 grams of potassium carbonate in 1 litre of water. (3) *N*:100- or *N*:200-thiosulphate solution. (4) 1% soluble starch, 2% potassium chloride solution. The weighed blood on the filter paper (about 0.1 gram) is extracted by 6.5 c.c. of

solution*1. The first extract is poured off, and a second extraction is made with 6.5 c.c. of the solution. Two c.c. of the iodate solution (No. 2) are then added, and the mixture is heated for exactly two minutes. Fifteen seconds before the end of this time, 2 c.c. of 20% (by volume) sulphuric acid are added. After cooling, potassium iodide solution (5%) is added, and titration is carried out by thiosulphate solution (No. 3), using starch (solution 4) as indicator. The difference between the result obtained and the titer of 2 c.c. of the original iodate solution gives the amount of sugar. 0.10 Mg. of dextrose is equivalent to 1.96 c.c. of N/200-thio-sulphate solution.

S. B. S.

The Microchemical Method of Estimating Dextrose. IVAR

BANG and K. HATLEHOEL (*Biochem. Zeitsch.*, 1918, **87**, 264—272).

—The authors find that exact timing of the heating for the reduction process in Bang's method (see preceding abstract) can be avoided by blowing a current of steam through the mixture for four minutes. A slight alteration must be made, however, in the solutions used, especially as regards the amounts of copper sulphate and alkali. The solution for extracting the filter paper containing the blood is as follows: 400 grams of potassium chloride, 3 grams of uranyl acetate, 1.5 c.c. of 25% hydrochloric acid, and 800 mg. of copper sulphate in 2 litres. The iodate solution contains 15 grams of potassium carbonate, 20 grams of potassium ammonium tartrate, and 0.3567 gram of potassium iodate in 1 litre.

S. B. S.

A Modification of the Selivanov Reaction [for Detection of Ketoses or Sucrose]. F. WEEHUIZEN (*Rec. trav. chim.*, 1918, **37**, 302—303; *Pharm. Weekblad*, 1918, **55**, 831—832. Compare A., 1887, 459).

—The reaction may be performed without heating the reacting mixture if a saturated solution of hydrogen chloride in absolute alcohol is used, and to it is added the mixture of sugars, under examination for the presence of a ketose or sucrose, and some resorcinol. A cherry-red coloration appears within three minutes. The method may be applied to the detection of sucrose in milk. [See, further, *J. Soc. Chem. Ind.*, 436A.] W. G.

Effect of Codeine in Hindering the Precipitation of Morphine by Ammonia from a Solution of its Lime Compound. H. E. ANNETT and HARDAYAL SINGH (*Analyst*, 1918, **43**, 205—213).

—The Pharmacopœia method for the estimation of morphine in opium consists essentially in mixing the sample with calcium hydroxide and water, filtering the mixture, and precipitating the morphine in the filtrate in the presence of ether and alcohol. Codeine also dissolves in the calcium hydroxide solution, and its presence diminishes the quantity of morphine precipitated subsequently by ammonia, the effect increasing with the concentration of the solution and of codeine. The codeine may, however, be removed by extracting the solution with toluene previously to

the precipitation of the morphine, and this modification is recommended in the estimation of morphine in opium, particularly in Indian opiums with a high codeine content. Narcotine is quite insoluble in water in the presence of an excess of calcium hydroxide, either alone or mixed with morphine and codeine. W. P. S.

[**Estimation of Histidine in Proteins.**] WALTER E. THRUN and P. F. TROWBRIDGE (*J. Biol. Chem.*, 1918, **84**, 355—356).—See this vol., i, 324.

[**Estimation of Quinine in the Organism.**] HEINZ HARTMANN and LORO ZILA (*Arch. exp. Path. Pharm.*, 1918, **83**, 221—234).—See this vol., i, 328.

Is the Adamkiewicz Reaction due to Glyoxylic Acid or to Formaldehyde? E. VOISENET (*Compt. rend.*, 1918, **166**, 789—792).—As opposed to the view of Hopkins and Cole (A., 1901, i, 310), the author considers that the colour reaction is due to the presence of formaldehyde and not of glyoxylic acid. A very dilute solution of formaldehyde readily gives the violet coloration in the presence of a trace of protein. The formaldehyde may be produced in the acetic acid by oxidation. W. G.

Effect of Time of Digestion on the Hydrolysis of Casein in the Presence of Starch. J. S. MCHARGUE (*J. Agric. Research* 1918, **12**, 1—7).—The Van Slyke method for protein analysis, when applied to mixtures of casein and starch, in the proportion of 1:5 which have been hydrolysed from twelve to fifteen hours with 20% hydrochloric acid, gives results for the amino-acid groups that are comparable with those obtained by Van Slyke for casein alone. Prolonging the time of digestion with this strength of acid on such a casein-starch mixture brings about a redistribution of the nitrogen in the histidine and cystine groups. The insoluble residue from the casein-starch hydrolysis contains nitrogen, which is in an inert form and should not be included in the human determination. W. G.

Mechanical and Physical Analysis of Soils. G. RICHTER (*Int. Mitt. Bodenk.*, 1916, **6**, 193, 318; from *Bied. Zentr.*, 1918, **47**, 49—52).—A discussion of the various methods for the mechanical and physical examination of soils; Kopecky's trituration method is preferred to that of Atterberg; Breitenbach's method for the estimation of the hygroscopic properties of soils gives higher results than those obtained by Mitscherlich's method. [See, further, *J. Soc. Chem. Ind.*, 384A.] W. P. S.

